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No. 1

THE ELECTRON IN CHEMISTRY.*†

BY

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THE MECHANISM OF CHEMICAL COMBINATION.

Let us in the first place consider chemical combinations between gases. That something more than collisions between the molecules of the reacting gases is required is clear, from the fact that gases like hydrogen and oxygen, hydrogen and chlorine (in the dark), which can form very stable compounds, can be mixed without any appreciable amount of chemical combination taking place at moderate temperatures. The test is a very severe one since at atmospheric pressure each molecule of oxygen in a mixture of hydrogen and oxygen would in one second collide with many million hydrogen molecules, so that even if only one collision in a million were to result in combination the rate of combination would be very great. A mixture of hydrogen and oxygen in the proportion of two molecules of hydrogen to one of oxygen can be stable, (*a*) when the gases are uncombined, and (*b*) when they are combined and the mixture exists as water vapour. The large evolution of heat observed in the transit from (*a*) to (*b*) shows that (*b*) has much less potential energy than (*a*). The fact that the gases can exist side by side without combination shows that

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the phase of high potential energy does not spontaneously pass to one of lower. We have many examples of this in ordinary mechanics. Thus the water in a mountain lake has more potential energy than it would have if it ran down into the valley, it does not do so because before it could get away work would have to be supplied to raise it above the level of the height immediately surrounding it. If a syphon is put into the lake this work is forthcoming and the water will run out. To enable a system to pass to a state of smaller potential energy may require the expenditure of a certain amount of energy and if this is not forthcoming the change will not take place. Thus, if a preliminary to the combination of hydrogen and oxygen were the dissociation of the molecules of these gases into atoms, the gases would not combine unless the very considerable amount of energy required for this initial stage were available. Now in the mixture of two pure gases the energy available is that due to the thermal agitation of the molecule; this at 0° C. is only about $1/30$ of a volt per molecule, and is small compared with the changes in energy occurring in chemical processes which on the same scale would be represented by several volts. Thus we might expect that unless some source of energy besides that due to thermal agitation were available, the combination would not take place. In the case we have just been considering, that of the dissociation of electrolytes in solution, the main part of the energy required to separate the ions in the electrolyte came not from thermal agitation, but from that derived from the falling in of polar molecules, *i.e.*, from the energy of chemical separation of the polar molecule and the molecule of the electrolyte.

The effect of water vapour, whose molecule is strongly polar, on the combination of gases is well known. Thus, H. B. Baker showed that very carefully dried HCl and NH_3 would not combine, that the combination of H_2 and Cl_2 went on exceedingly slowly, even in strong sunlight, when the gases were carefully dried, while H. B. Dixon showed that electric sparks might be passed through a mixture of dry CO and O_2 without combination taking place. He also showed that other substances besides water vapour render possible the combination between CO and O , and it is probable that all polar molecules possess this property to a greater or less extent. Baker found that the effect of water vapour was not confined to combination if extended also to dis-

sociation, for while ordinary ammonium chloride is dissociated to a very considerable extent when the temperature is raised to three or four hundred degrees centigrade, no dissociation occurs at these temperatures if the salt is very carefully dried.

When polar molecules, such as those of water or ammonia, are present, they may combine with the other molecules, forming aggregates in which, as in the case discussed in a previous lecture, there is a kind of incipient ionization, the atoms being more widely separated than in the normal molecule. The aggregate has a finite electrical moment and thus exerts much greater forces on neighbouring molecules than the normal molecule. Let us represent these aggregates by $A(H_2O)_n$, $B(H_2O)_m$ when A and B represent molecules of the reacting gases. When two of these come together the work required to separate them may be so much greater than that required to separate AB that though A and B cannot by collision form a potent aggregate $A(H_2O)_n$ and $B(H_2O)_m$ are able to do so. After the aggregate has been formed the atoms, loosened by the action of the polar molecules, rearrange themselves so as to produce the system with the minimum potential energy. If, as the result of this rearrangement, the water is set free, it will be available for producing a further supply of the complex molecules. Even if only a small percentage of the molecules are in the complex state the rate of combination might be considerable, as the number of collisions made by a molecule under ordinary circumstances is so large. Thus to take the combination of gaseous HCl and NH_3 to form NH_4Cl as an example. If even only one molecule in a hundred thousand were in the complex state and if the combination only occurs when a complex molecule of HCl collides with a complex one of NH_3 , these collisions will still be so numerous that something like one per cent. of the HCl and NH_3 will combine per second. We see from this that to avoid appreciable combination the gases must be exceedingly dry, and that traces of water too small to be detected by other means might produce very marked effects on chemical combination.

On this view of chemical combination the rearrangement of the atoms takes place inside a complex formed with the polar molecules, thus no ions need get free. There is very strong evidence against the necessity for the existence of free ions in gaseous combinations; free ions make a gas a conductor of electricity and the conductivity due to free ions can be detected when the number

of free ions is much less than one-million-millionth of the number of molecules. Many cases of chemical combination have been tested for electrical conductivity without any trace of it being detected. Thus L. Bloch¹⁸ showed that many chemical actions which go on at moderate temperatures, such as the oxidation of nitric oxide, the action of chlorine on arsenic, the oxidation of ether vapour and so on, have no effect on the electric conductivity of the gases. I found, too, that even when the combination was as vigorous as that between hydrogen and chlorine in the light, no effect whatever was produced on the electrical conductivity of the mixture. Again dissociation at moderate temperatures such as that of nickel carbonyl at about 100° C. into nickel and carbon monoxide, or in the dissociation of arseniuretted hydrogen, is quite without effect on the conductivity. This is in accordance with the consequences of the theory.

There are, however, some cases in which free gaseous ions are produced by dissociation or chemical action. Thus Kalendyk¹⁹ found that the vapour of potassium iodide was a conductor of electricity at temperatures above 300° C. if damp, but not when dry; this is a good example of the effect of water vapour. Another case investigated by Bloch (*loc. cit.*) is the oxidation of P_2O_3 to P_2O_5 , which is also accompanied by an increase in electrical conductivity.

The efficacy of polar molecules is on this view due to their large electrostatic moment, which causes them to be strongly attracted by other molecules. Any systems, such as free electrons or gaseous ions, which give rise to strong electric fields, might be expected to promote chemical combination by processes similar to those which occur with water molecules.

Again, if the reacting gases were condensed on the surface of a piece of metal, or on the surface even of a non-metal or liquid, particularly if these substances were of special types, the molecules would find themselves in the presence of agents of the kind we are considering. At the surface of a metal there are mobile electrons, while the molecules at any surface can only be coördinately saturated in very exceptional cases. For when a new surface is produced by fracture some of the atoms which helped to "satisfy" the molecules left behind have been torn away, so

¹⁸ *Annales de Chimie et de Physique*, 22, pp. 370, 441; 23, p. 28.

¹⁹ *Proc. Roy. Soc.*, A90, p. 638, 1914.

that the molecules on the surface must be unsaturated and able to bind other atoms or molecules. The energy derived by the approach of a molecule to the unsatisfied molecules at the surface of the solid or liquid may be used to separate the atoms in the approaching molecule, in just the same way as the energy due to the approach of a polar molecule helped to separate them. Thus the molecules of a gas condensed in a layer on a surface will be exposed to influences very similar in character to those to which they would be exposed when combined with water molecules, and we may expect to find that the connection between these atoms gets so loose that these are able to rearrange themselves and form new compounds.

The layers condensed on a surface will in many respects be in a more favourable condition for entering into chemical combination than the free molecules of the gas, even if these are supplied plentifully with water molecules. For the molecules in the surface layer will be crowded together and kept in close contact; they will thus be in a situation particularly favourable for the rearrangement of their atoms.

The effect of metal surfaces in promoting chemical combination is shown by the combination of hydrogen and oxygen produced by platinum black, by the synthesis of ammonia in the Haber process, by the effect produced by metals when in the colloidal state, by the Sabatier-Senderens method, where many changes in organic compounds are produced by passing them along with hydrogen over finely divided nickel or certain other metals at a high temperature. Another instance is the effect produced by the walls of the vessel in which the reacting gases are contained; many examples of this are given by Van t'Hoff in his studies on chemical dynamics.

It is possible that water in addition to the effect it produces by its individual molecules may produce an additional effect by forming small drops, which in the aggregate might have a very large surface, on which the gases might condense.

We can get some very direct evidence as to the conditions at the surface of separation of gases, liquids and solids by the study of the very interesting cases of electrifications produced by the bubbling of gases through liquids, by the splashing of liquids against solid surfaces, and the motion under an electric

field of bubbles of air, and colloidal particles through liquids. When gases bubble through certain liquids of which water is a conspicuous example, the gases after they emerge from the liquid are found to be electrified. The liquids which give rise to this electrification are those which possess considerable electrical moments, *i.e.*, they are those which, as we have seen, have the property of forming complex compounds with compounds which are already electrically saturated. The amount, and even the sign of the electrification produced by bubbling, is very sensitive to small changes in the composition of the liquid. Thus air bubbling through pure water emerges with a negative charge, but if a small quantity of HCl or H_2SO_4 be added to the water, the electrification of the air becomes positive. The electrification is dependent upon the breaking of the liquid film when the air bubble escapes from the fluid. No electrification is produced by blowing a current of air along a water surface or by stretching, without breaking, a liquid film. A similar dependence upon the composition of the liquid is shown by the motion through a fluid of small particles or air bubbles under an electric field, a phenomenon which is sometimes called cataphoresis. The addition of acids and salts, especially if these contain elements of high valency, produces a great effect on the velocity with which the bubble moves through a liquid under a constant electric field. Cataphoresis is more amenable to mathematical treatment than electrification by bubbling and the mathematical theory has been worked out by v. Helmholtz and Lamb on the supposition that there is a double layer of electricity, one layer being positive and the other negative, at the surface between the bubble and the liquid, and that one layer is attached to the liquid, the other to the bubble or colloidal particle. If v is the velocity of a particle under an electric force X , η the coefficient of viscosity of the liquid, σ the surface density of the electric charge on either layer, d the distance between the layers, then according to v. Helmholtz

$$v = \sigma dX/\eta \quad (29)$$

so that the measurement of the velocity would at once give us the potential difference at the surface. Lamb has given very strong reasons for thinking that this relation is not sufficiently general and is based upon suppositions which are not likely to be valid when, as in this case, we are dealing with distances which are of

the order of atomic distances; he finds instead of (29) the equation

$$v = \sigma l X / \eta \quad (30)$$

where l is a length dependent on the liquid and on the nature of the particle. As l is not known, we cannot claim that the use of the v. Helmholtz formula gives more than the order of the surface density, in some cases, however, where it has been possible to measure the potential difference between the particle and water, this has been in fair agreement with the value deduced by Helmholtz's equation. It will be noticed that according to either formula the velocity of the particle is independent of its size, provided σd and σl are unaltered. This has been verified by several observers, among others by Burton²⁰ and McTaggart.²¹ In water, air bubbles and some solid particles move as if the negative charge were on the particle, and it is remarkable that, in spite of great variations in the character of the particle, the changes in the potential difference are comparatively small. This is shown in the following table taken from Burton.²² The potential difference φ has been calculated from the v. Helmholtz equation assuming

$$\varphi = 4 \pi \sigma d / K$$

where K is the specific inductive capacity of water.

Substance.	Potential Difference in Volts Deduced by Helmholtz's Equation.
Lycopodium	-.035
Quartz	-.042
Air bubbles	-.056
Arsenious sulphide	-.031
Prussian blue	-.056
Gold (Bredig)	-.030
Platinum (Bredig)	-.028 - .034
Silver (Bredig)	-.033
Mercury (Bredig)	-.035
Bismuth (Bredig)	+.015

We see from this list that for many substances the difference of potential between the two layers is about 1/30 of a volt: this is very nearly the potential difference through which an electron must fall at room temperatures to acquire an amount of energy equal to that possessed by a molecule of gas from its thermal

²⁰ "Physical Properties of Colloids," 2nd Edition, p. 136.

²¹ *Phil. Mag.*, **27**, p. 297 (1914).

²² "Physical Properties of Colloids," p. 135.

agitation. Thus a charged atom at the double layer would possess by thermal agitation an amount of energy comparable with that required to detach it from the double layer. We should expect that a limit to the potential difference between the two layers must be imposed by the necessity of one layer being able to move freely relatively to the other. If, for example, the double layer were formed by positively and negatively charged atoms in the same molecule it could not produce cataphoresis unless some source of energy sufficient to dissociate the positive from the negative parts were forthcoming. If this energy has to come from thermal agitation, the positive and negative parts must have been driven so far apart that the energy required to separate them is of the order of the mean kinetic energy of a molecule due to thermal agitation, which at 0° C. is about $1/30$ of a volt. The energy required to detach a charge from the double layer is proportional to the potential difference between the layers. Thus the energy available from thermal agitation may be a most important factor in determining the value of the potential difference in the effective double layer.

THE FORMATION OF THE DOUBLE LAYER.

Polar molecules, such as those of water, have, as we have seen, the power of forming molecular compounds in which oppositely charged atoms are separated and put into a condition in which they can be easily detached from each other. These compounds are of two types, in the first symbolized by such a case as $[\text{Me} \cdot 4\text{H}_2\text{O} \cdot (\text{OH})_2]\text{H}_2$, the effect of the formation of the complex compound is to give a charge of negative electricity to the substance with which the water is in contact and to put two positively charged atoms into a condition in which they can easily be detached from the substance. The formation of a compound of this type would produce a double layer with the positive part in the water and the negative on the substance. This is the type of double layer formed at the surface of colloidal particles of platinum, gold, silver, quartz or air bubbles. The other type of complex compound is that symbolized by $[\text{Ca} \cdot 4\text{H}_2\text{O}]\text{Cl}_2$, here the water molecules drive out the negative constituent from the original compound and give to the system surrounding the central atom a positive charge. If a substance of this kind were formed there would again be a double layer, but in this case the negative

part of it would be in the water, the positive on the substance in contact with the water. This is the type of double layer formed at the surface of colloidal particles of ferric hydroxide.

The case of a gas bubble in water is an interesting one in which the evidence on some points is somewhat conflicting. McTaggart found that the velocity of bubbles of hydrogen was the same as that of oxygen bubbles indicating that the potential difference was independent of the nature of the gas, and that the gas did not take part in any chemical reaction. Alty, who has recently been making experiments on this point in the Cavendish Laboratory, finds that considerable variation in the velocity of the bubbles is produced in some cases by changing the gas. The view that oxygen may take part in chemical reactions with water is supported by the observation frequently recorded but first made, I think, by Bellucci,²³ that the air in the neighbourhood of waterfalls, where there is a great deal of splashing, contains abnormally large quantities of ozone. Under the action of the water molecules ozone may be formed and negatively electrified ozone form the coating in the gas of the double layer.

We should expect that there would be a double layer at a surface separating water from its own vapour. Hardy and Langmuir have pointed out that the molecules at a liquid water surface are polarized, *i.e.*, the number of molecules which have their positive ends at the top is not the same as the number with the negative end. Thus, suppose the majority of molecules had the negative ends, *i.e.*, the oxygen atom, at the top, the oxygen atoms are not coördinately saturated and may combine with the molecules of water vapour to form compounds of the type $[\text{O.H}_x](\text{OH})_x$: This would give rise to a double layer with the positive half in the water, the negative one in the bubble. Experiments are in progress at the Cavendish Laboratory to see whether any evidence can be obtained of a double layer when water is in contact with nothing but water vapour.

The formation of the double layer gives a supply of positive and negative ions at the surface of an air bubble in water. Just before the bubble emerges from the water this surface has a considerable area. It is reduced to very small dimensions after the bubble emerges. Thus the emergence of the bubble involves a

²³ *Ber. Deutschen Chem. Gesell.*, **8**, p. 905 (1875).

considerable and very abrupt contraction of the surface and of the double layer associated with it. The double layer will be violently distorted and it does not seem surprising that some of the ions in the layer on one side should not have time to combine with those on the other before they are carried away by the air. Only a very small fraction of the ions in the double layer get liberated when air bubbles through water. Assuming v. Helmholtz's formula, we can calculate from the velocity of the bubble the quantity of electricity per unit area of each layer. Assuming that the distance between the layers is 10^{-8} cm., McTaggart (*loc. cit.*) found that this density was 4×10^{-5} coulombs per square centimetre. If all the water molecules had been polarized, *i.e.*, if all the OH ions of the water molecules were next the surface and if the distance between two molecules of water on the surface were the same as that in the interior, *i.e.*, 3.09×10^{-8} cm., the density would be about 1.7×10^{-4} coulombs per square centimetre, about four times greater. On one layer of a bubble 7.8 mm. in diameter the charge on either layer would be 7.6×10^{-5} coulombs. Simpson²⁴ found that when a drop of this size struck against a plate the amount of electricity set free was 2.8×10^{-12} coulombs, *i.e.*, only about one thirty-millionth of the charge on the layer. We conclude from this that only an exceedingly small fraction of the water molecule at the surface of an air bubble or drop of water is ionised by the bursting of the bubble or the splashing of the drop.

When air bubbles through water some ions become free, there are other types of experiments when, though there is a separation of positive and negative electrification, few if any ions get free. The Armstrong hydro-electric machine is a case in point. Here small drops of water are carried by a jet of steam through a tube with great velocity. In their passage through the tube the drops strike against the sides and the tube becomes negatively, the drops positively, electrified. Here the separation of the positive and negative electrification is the principal effect and not the liberation of free ions. We have supposed that at the surface of a drop of water there is a double layer, the negative part, OH ions, in the air and the positive part, H ions, in the water. When the drop strikes against the tube the OH ions combine with the material of the wall of the tube forming those

²⁴ *Phil. Trans.*, 209A, p. 379 (1909).

molecular compounds we have been considering in this chapter. When the drop rebounds from the wall of the tube it will tend to take the H_+ ions away with it, while the walls of the tube will hold the OH_- ions. The ions will be separated by the kinetic energy of the drops. The ions will not, however, get free; the positive ones will be on the water drops and the negative ones on the walls of the tube. This is a particular case of electrification by friction, and it is evident that the formation of double layers must be of vital importance in that phenomenon

ACTIVE MOLECULES.

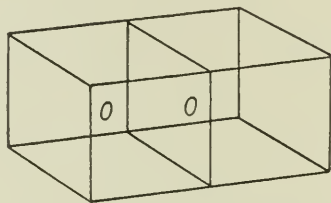
We have hitherto considered the way in which chemical combination was promoted by polar molecules and by active surfaces, the energy necessary for the preliminary separation of the atoms in the reacting molecules before their final readjustment to form the molecules of the new compound coming from the potential energy of separation of the polar molecules and of the reacting molecules before combination. We have seen that the kinetic energy of thermal agitation is inadequate for this purpose. Though the influence of polar molecules on chemical combination is undoubtedly very great, the evidence does not, I think, warrant the conclusion that all chemical combinations are dependent upon their agency. The combustion of carbon bisulphide, of cyanogen and of certain hydrocarbons in oxygen appears to be unaffected by the presence of traces of moisture.²⁵ The question arises, what is the mechanism by which the combination can be brought about, when the energy arising from polar molecules is not available, and when that due to thermal agitation is too small to split up the molecules of the reacting gases into atoms? The electron theory indicates a way in which certain molecules could be put into a chemically active state without separation into atoms by an expenditure of energy much less than would be required for that purpose. Consider, for example, a molecule of oxygen, its neutrality is attained by the arrangement of its electrons into two octets, to obtain these two the utmost economy in construction must be observed and the octets have to have four electrons in common. Let the electrons in the molecule be displaced so that the cells surrounding the atoms have no longer four electrons in common, suppose, for example, that they have only two in com-

²⁵ H. B. Baker, *Proc. Manchester Phil. Soc.*, 53, No. 16.

mon, then since there are only twelve electrons available there can only be seven electrons in each cell, and each atom will be surrounded by only seven electrons instead of by eight. Now the cell of seven electrons is not saturated and will be chemically active, though it will not be so unsaturated as the free oxygen atom which is only surrounded by six electrons. To move the electrons so as to change the arrangement of electrons from that corresponding to the inactive state represented by Fig. 34 to that of the active state represented by Fig. 35 would require far less energy than to separate the atoms, so that the necessary amount may be derivable from thermal agitation at temperatures far below that required to separate the atoms.

I think this conception of the active molecule has an important bearing on the combination of explosive mixtures such as those of

FIG. 34.



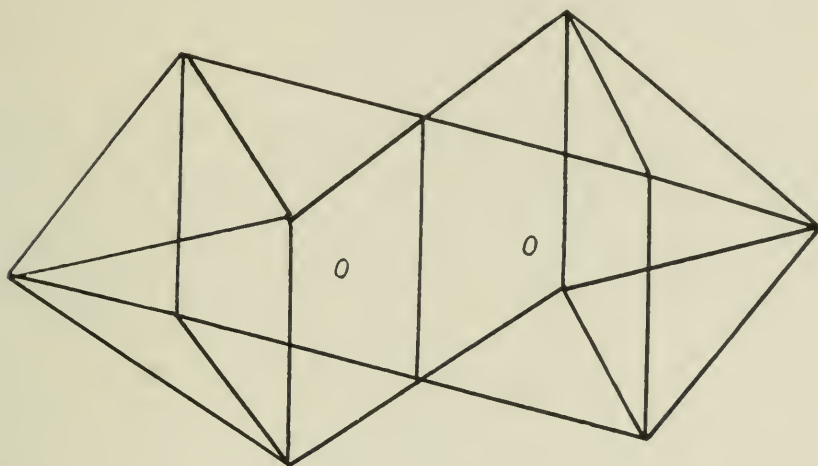
oxygen and hydrogen; these gases explode at temperatures as low as 600° C. where the energy of thermal agitation is quite insufficient to split the oxygen molecules up into atoms. Indeed, direct experiments on the relation between temperature and pressure have shown that there is no appreciable dissociation of the molecules of oxygen at 1700° C. If, however, the work required to make the molecule active in the manner described was that corresponding to thermal agitation at a lower temperature, say 600° C., then if in any region of a mixture of the explosive gases the temperature reaches this value, the oxygen molecules will become active and combine with the hydrogen, the heat developed by the combination will raise the temperature still further and the hot molecules will travel out with energy sufficient to make the molecules of oxygen against which they strike active. This will lead to further combination and a further development of heat and combination will spread throughout the mixture.

As there is no dissociation of the molecules into atoms, the process of making the oxygen molecules active will not change the pressure in pure oxygen.

There is direct experimental proof that the molecule of oxygen can be put into the active state. When we use the method of positive rays we find that oxygen is one of the few molecules, as distinct from atoms, that can occur with a negative charge. If the oxygen molecule could only occur with its electrons arranged as Fig. 34, it could not receive a negative charge, because there is no room for an electron in the octets. It could, however, receive such a charge if the electrons were arranged as in Fig. 35 because there is room for an electron on each of the septets.

The fact that a particular atom or molecule can be negatively charged, shows that it can be in stable equilibrium after receiving

FIG. 35.



an additional electron, so that in the neutral state it is unsaturated and chemically active.

The arguments we have used about the oxygen molecule will apply to any arrangement of electrons where there are two octets with four electrons in common. This arrangement occurs when we have two atoms connected by a double bond—it occurs, for example, in carbon compounds whenever there is a double bond between two carbon atoms, $C=C$, it also occurs in the combination $C=O$, though not in $C-O-H$.

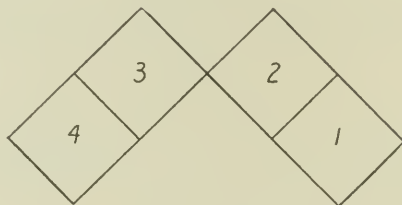
THIELES' THEORY OF PARTIAL VALENCIES.

This conception of the active molecule leads in many cases to the same results as Thieles' theory of partial valencies. Thus to take the case which led to the theory. It was found that a compound where the carbon atoms are arranged according to the

scheme $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{C} - \text{C} = \text{C} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \end{array}$, where two double bonds are separated by a single one, when it forms additions compound does so by adding the new atoms to the carbons at the *ends* of the chain. On our view the distribution of the electrons in the compound is represented in Fig. 36.

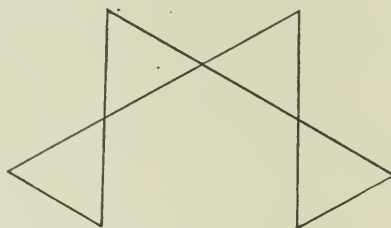
There are four octets, 1, 2, 3, 4; 1 and 2 and also 3 and 4 have four electrons in common, 2 and 3 only two. Suppose all the

FIG. 36.



carbon atoms get put into the active condition. The octets with four electrons in common will become septets with two electrons in common and the system will be a chain of four septets (Fig. 37), where the septets are represented by triangles, each having two electrons in common with its nearest neighbour. To

FIG. 37.



make this change in which all the carbon atoms have been made active requires the expenditure of a certain amount of energy; an expenditure of a smaller amount will be sufficient to make a part of them active. To find the change which will require the least energy, we notice that if any adjacent pair of septets were to revert to a system with four electrons in common, the new system would have less potential energy than that shown in Fig. 37, and would require less energy to be expended to derive it from the original system.

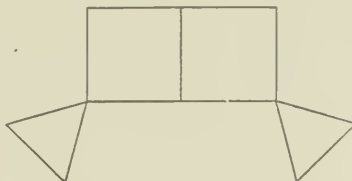
The work required for this change would be the work required to convert the system (Fig. 36) into the system (Fig. 37), minus the loss of potential energy when an adjacent pair of septets

reverts to two octets with four electrons in common. Thus the system which will require the minimum work will be the one when the pair which reverts is the one for which the loss of potential energy on reversion to octets is greatest. This pair will be the one which is most symmetrically placed, *i.e.*, the central pair. Thus the active configuration which requires the least expenditure of work is that represented in Fig. 38, where the end cells are septets and active. As these cells are active, additions will take place at them, and the central carbons will be connected by a double bond.

KETO-ENOL CHANGE.

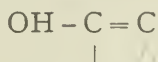
The same reasoning will apply where the double bond is between a carbon and an oxygen atom. Thus in the compound

FIG. 38.



$O = \underset{\substack{| \quad \wedge}}{C} - C - H$, the distribution of electrons is that represented

in the figure, if the two octets with four electrons in common are made active, the active oxygen units with the neighbouring atom of H, the hydrogen coming away from C_2 with its electron; this completes the octet round O, leaving septets round C_1 and C_2 with two electrons in common; these revert to the more stable arrangement of the same number of electrons, *viz.*, two octets with four electrons in common, and we have thus the compound



this is known as the keto-enol change. It only takes place when one of the atoms attached to C_2 is that of an electronegative element; the reason for this follows from the same considerations as those previously given to explain the effect of introducing electronegative groups into hydrocarbons.

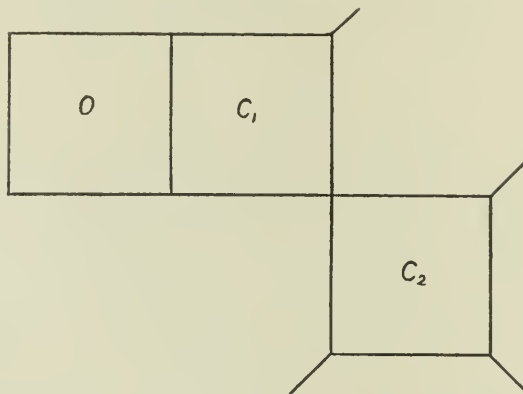
The same principles will apply to a smaller extent when two octets have only two electrons in common, for if the electrons were displaced so that the cells had only one electron in common, one of the atoms would become active and could enter into chemi-

cal combination. Thus, if the electrons in a chlorine molecule get displaced so that the cells have only one electron in common instead of two, one of the cells will become active and can combine with hydrogen. The energy required to displace the electrons need not come from the energy of thermal agitation, it might come from light if that were absorbed by the molecules.

PRODUCTION OF LIGHT BY CHEMICAL CHANGE.

Many chemical reactions involve an increase or a decrease in the number of electrons grouped round some of the atoms; thus, for example, if an atom of hydrogen combines with one of

FIG. 39.



chlorine to form HCl, after combination the chlorine atom is surrounded by eight electrons, whereas before it was surrounded by only seven, thus the reaction has resulted in an electron falling into the layer round the chlorine atom; this atom may be regarded as coming from the hydrogen atom. On the other hand, when HCl dissociates into H and Cl the chlorine ion loses an electron, while the hydrogen ion gains one. We shall use the term oxidation for the process by which the atom of an electronegative element gains an electron and becomes negatively charged since ordinary oxidation is a process of this kind, and reduction for the process by which a positively electrified ion of an electropositive element receives an electron and becomes neutral.

Thus, in oxidations an electron falls into the zone round the atom of an electronegative element; in reductions an electron falls into the zone round the atom of an electropositive one. From the study of the luminous effects in the discharge of electricity through gases we are led to the conclusion that the capture of

an electron by an atom results in the emission of light, and from the quantum theory it would follow that the frequency of the light would be proportional to the potential energy lost when the electron falls into the atom, or what is equivalent, to the work required to remove an electron from the negatively electrified constituent of the compound in the case of oxidation or from the neutral atom in that of reduction. Thus we should expect that both oxidation and reduction would be accompanied by the emission of light; it may be that the rate at which the chemical processes go on is so slow that the energy in the light is not sufficient to make it apparent, or again, that the wave-length of the light is not within the range of the visible spectrum. The production of light by chemical action is a well-known phenomenon. In addition to the conspicuous cases of flames where the temperature is high, there are many examples of luminosity occurring at moderate temperatures; the luminosity of phosphorus when oxygen passes over it is one example; then there is the luminosity of sulphur when heated to about 300° C. in the presence of oxygen, the light given out by the glowworm and by the animalculæ which cause the phosphorescence of the sea. Linneman found that fresh surfaces of sodium or potassium are luminous in the dark until they get covered by a coat of oxide. This production of light is, I think, the cause of the emission of electrons in the dark from the alloy of sodium and potassium when exposed to various gases which I observed many years ago and which has been investigated very fully by Haber. If chemical action went on between the gases and the NaK alloy, light would be given out, and as the alloy is very photoelectric, electrons would be given out by the surface of the alloy. The seat of the light is at the surface of the alloy so that, although the light might not be intense enough to be visible at molar distances, yet at the atomic distances which separate it from the alloy its intensity might be sufficient to produce very considerable effects. Again, since in oxidations the origin of the light is in the electronegative elements, we should not expect to find in light due to oxidation the spectrum of the electropositive element. It has long been considered remarkable that the spectrum of hydrogen is not visible in flames or in light produced by chemical means, though it is so easily produced by the electric discharge. This is just what we should expect if the chemical reactions were of the type of oxidations; to have

a chance of getting the hydrogen spectrum the process should be a reduction. Thus, for example, in the partial dissociation of hydroiodic acid, when there is equilibrium between the formation of HI and its dissociation into H and I, the combination would give rise to the spectrum of HI with the iodine as the source of light, the dissociation might give the hydrogen spectrum. It is to be noted that the spectrum of a molecule may vary with the atom in that molecule which is excited. Thus to take as an example COCl_2 , the spectrum emitted due to the fall of an electron into the oxygen atom would not be the same as that due to the fall of one into the chlorine atom. We have in considering the type of light emitted to consider not merely the atom into which the electron falls, but also the method in which it falls. Thus to take a case in which we have very vigorous reduction going on, that of the liberation of hydrogen from the cathode when strong currents pass through acidulated water. Since the hydrogen atoms which come off are neutral, the hydrogen ions which were positively electrified must each have received an electron and so might be expected to have given out light. I am not aware, however, that anyone has observed any luminosity in the neighbourhood of the cathode during the electrolysis of acidulated water. Nor need we, I think, expect it; we have already seen reasons for thinking that hydrogen ions in water have attached to them a number of water molecules, the negative ends of these molecules being turned towards the hydrogen ion. The effect of these negative charges is to diminish very materially the attraction of the hydrogen ion on the negative electron, so that when the electron falls into the ion it will do so with very much less energy than it would in the absence of the water molecules; as the energy is so much less, the intensity of the light and also its frequency will be greatly diminished, so that not only will the light be feeble, but also probably far away, on the red side of the visible spectrum.

ON HOMOLOGOUS ELEMENTS AND VARIABLE VALENCY.

Homologous Elements.—The valency of an element depends according to these views on the number of electrons in the outer layer rather than upon the total number of electrons in the atom. We have supposed that the electrons in the atom are arranged in a finite number of layers, the members of each layer being approximately at the same distance from the centre of the atom.

As we pass from the atom of one element to that of the element next in order of atomic weight, we have to provide for the accommodation of one more electron in the atom. If the additional electron joins those in the outer layer it will give rise to an atom of an element of different valency and with very pronounced difference in chemical properties. If, however, the electron finds accommodation in one of the layers below the surface, the element corresponding to this atom will have the same valency as the first and will resemble it in chemical properties more or less closely according as the layer on which the new electron settles is near to or far from the centre of the atom. Thus we might have a graduated series of elements differing in atomic weight; the properties of some—those with the additional electrons in the layers close to the centre differing so little from those of some element of smaller atomic weight in the series that the two might with propriety be regarded as isotopes. The difference in properties will increase though the valency remains unaltered, as the electrons find a place in layers nearer the surface until finally we come to the element where the additional electron has got to the outer layer; here there is a change in the valency and a marked alteration in the chemical properties. We are thus led to expect the existence of groups of elements possessing very similar properties; in some cases the chemical properties might be so similar that the elements would not be separable by chemical means and would be classed as isotopes; in others the differences would be large enough to enable the elements to be isolated by chemical processes. Examples of such groups are the iron, nickel and cobalt group, the ruthenium, rhodium and palladium group, the large group of the rare earths and the iridium platinum group. Inside these groups, increase in atomic weight is not accompanied by change of valency; outside them, it is.

In considering the way in which a definite number of electrons will arrange themselves round a central charge, there are two influences of predominating importance: The first of these is the tendency of the electrons to get as close to the central charge as is consistent with the stability of the layer, *i.e.*, to have as many electrons in the innermost layer as the central charge can hold in stable equilibrium, and then as many in the second layer as the central charge when surrounded by the first layer can hold in stable equilibrium, and so on. This disposition will make the

potential energy due to the forces between the positive nucleus and the electrons as small as possible. The potential energy due to the forces between the electrons has next to be considered. This will diminish as the distances between the electrons increase and will tend to make the electrons in the various layers arrange themselves so that their figures are similar, or at any rate have the same kind of symmetry about the centre. This latter tendency would, if it prevailed, cause a new electron if added to an atom already containing a number of electrons either to go to the outer layer, or if that were full, to make the beginning of a new outer layer. The tendency to get as close as possible to the centre would, on the whole, make for the retention of the electron by one of the inner layers.

We should expect that we could not go on increasing the number of electrons without reaching a stage where a new electron would stay in the inner layers. If so, its influence on the chemical properties would be very slight and the new element would be very similar to the old. The addition of an electron to one of the inner layers would alter the nature of its symmetry round the centre and make it different from that of the other layers; as the different layers like to have the same kind of symmetry, when one layer has got a new electron the others will try to get one, too, so that when once the absorption of electrons by the inner layers has begun it will continue as the next few electrons are added to the atom. When each layer has received an electron, we may expect the next electron to come to the surface, giving rise to an element whose properties are markedly different from those of the elements which just preceded it. Thus the homologous elements might be expected to occur in groups and inasmuch as in the elements inside the group, some of the layers have one kind of symmetry and others a different one, the distribution of electrons inside the atom of elements in a homologous group is irregular and does not possess the uniformity or regularity possessed by elements outside the group where the electrons in the inner layers have adjusted themselves so as to produce a high degree of symmetry.

Varying Valency.—We have been considering cases where different elements have very similar chemical properties, although they contain different numbers of electrons, where, in fact, we have variations in the number of electrons in the atom without

much alteration in the chemical properties. The question naturally arises whether we might not have also variation in the chemical properties without alteration in the number of electrons, and whether the existence of some elements which have more than one kind of valency is not a case in point. Ferrous and ferric iron have different properties, so have cuprous and cupric copper. As the elements can pass backwards and forwards between the -ous and the -ic states, if these states correspond to two different configurations of the same number of electrons, these configurations must be such that by suitable chemical or physical processes they can pass from one form to the other. We have already seen that there are frequently more ways than one of arranging in stable equilibrium a given number of electrons round a central positive core. If these arrangements are to explain the difference between the -ous and -ic states of the elements, they must differ in the arrangement of the outer layer (*a*) because unless they did so there would not be sufficient difference in the chemical properties in the two states, and (*b*) because if the difference was only in the inner layers we could not affect these sufficiently by ordinary chemical operations to cause one configuration to pass into the other.

We should expect, I think, to find forms of the same kind of atom differing in their outer layers in those elements which are either in a group of homologous elements or in their immediate neighbourhood. For in the atoms of such elements an electron hesitates, as it were, whether to go to the surface or to stay in one of the inner layers, *i.e.*, it hesitates between two different configurations. It is reasonable to suppose that by suitable influences at the surface the electron might be induced to take one course or the other and thus confer one valency or another on the atom of which it is an occupant. Now it is remarkable that many of the elements which are most conspicuous for the variability of their valency are either in the homologous groups or in their immediate neighbourhood. Take, for example, chromium and manganese, which are the next neighbours of the iron groups. each of these shows great variations in valency in its different compounds, then molybdenum, the next neighbour to the ruthenium, rhodium and palladium group forms the series of chlorides MoCl_2 , MoCl_3 , MoCl_4 , and MoCl_5 ; again tungsten, the next neighbour to the platinum and iridium group, forms the four

chlorides WCl_2 , WCl_4 , WCl_5 and WCl_6 , and nearly, if not quite, all of the elements in the homologous groups themselves form more than one series of salts. The electrons in the outer layers of elements of this type seem to be in a peculiarly sensitive condition and can move from one layer to another without much expenditure of energy.

The number of electrons which can be held in stable equilibrium in a single layer by a positive charge increases with the charge. Thus, though an inner layer of eight might be as many as the positive charge possessed by the lighter elements could stabilize, yet the heavier elements with their large positive charges might be able to stabilize more than this number. We should thus expect that at some stage in the list of elements the number of electrons in the inner layers would increase, that while when we pass from one element to the next and the number of electrons in the atom increases the additional electron stays in the inner layer instead of going to the one on the outside of the atom. When this process begins the change from atom to atom will not be the addition of an electron to the outer layer, but a reorganization of the distribution of electrons in the interior of the atom. The properties of the elements indicate that this process begins soon after passing calcium. To illustrate the point, I will take the series of elements beginning with titanium and consider the arrangement of electrons in it and the neighbouring elements. I do not lay any stress on the actual numbers of electrons assigned to the inner layers; the determination of these would require much further investigation, both theoretical and experimental.

Titanium.—The distribution of electrons, if it followed the same course as in the lighter elements, would be represented by 2, 8, 8, 4, the figures representing the number of electrons in the different layers starting from the inside; the four electrons in the outer layer would make the element quadrivalent. The existence of the tetrachloride TiCl_4 shows that this distribution is one which occurs in nature. In addition to the tetrachloride there are the chlorides TiCl_3 , TiCl_2 , showing that forms of the titanium atom exist in which there are respectively one and two more electrons in the inside than in quadrivalent titanium, the distribution of electrons in the tautomeric forms may be represented by 2, 9, 8, 3, and 2, 10, 8, 2, respectively.

Vanadium.—If the electrons had followed the normal course,

the arrangement of the electrons would be represented by 2, 8, 8, 5, and the element would be pentavalent. Vanadium is said to form a pentafluoride VF_5 , so that this configuration would seem to exist. Vanadium forms chlorides VCl_4 , VCl_3 , VCl_2 , in which the inner layers of the atom must contain respectively one, two and three electrons more than the preceding case; thus we have atoms in which the arrangements are 2, 9, 8, 4; 2, 10, 8, 3; 2, 10, 9, 2, respectively.

Chromium.—If the electrons followed the normal course the arrangement would be 2, 8, 8, 6, and the element would be hexavalent; the compound CrF_6 shows that this type exists. Chromium forms the chlorides CrCl_3 , CrCl_2 , so that in addition there are atoms of the type 2, 11, 8, 3; 2, 12, 8, 2, respectively.

Manganese.—The normal arrangement would be 2, 8, 8, 7. The fluoride MnF_7 shows that this type exists. There are in addition the fluorides MnF_4 , MnF_3 , MnF_2 , corresponding to atoms of the type 2, 11, 8, 4; 2, 12, 8, 3; 2, 12, 9, 2.

Iron, Nickel and Cobalt.—From the similarity of these elements we infer that the distribution of electrons only differs in the inner layer. Their halogen compounds are all of the type FeCl_2 or FeCl_3 ; suggesting the following distribution of electrons:

Fe2, 12, 10, 2.	2, 12, 9, 3
Ni2, 13, 10, 2.	2, 13, 9, 3
Co2, 14, 10, 2.	2, 14, 9, 3

Copper.—The halogen compounds are of the type CuCl , CuCl_2 , indicating atoms with one or two electrons, respectively, in the outer layer, corresponding to distribution of electrons represented by 2, 14, 12, 1; 2, 14, 11, 2.

The normal process by which, when we pass from one element to the next in order of atomic weight, the new electron goes to the outer layer seems to be resumed after passing copper, thus we have zinc with two electrons in the outer layers; gallium with three; germanium with four; arsenic with five; selenium with six; bromine with seven, and krypton with eight.

Thus we see that as we proceed up the list of elements we may expect to meet with a batch of elements in whose atoms the electrons change from one tautomeric distribution to another with but little expenditure of energy. In this batch the ordinary progress of valency with atomic weight is interrupted, and the

valencies are variable. On passing through the batch the regular sequence is resumed, the series goes on and ends with eight electrons on the outer layer, while the next series begins with one in that layer.

Paramagnetism.—One very conspicuous feature of the elements from titanium to copper is that they are strongly paramagnetic. The quality of paramagnetism would on several theories depend on a want of symmetry in the arrangement of the electrons in the atom. This would be the case, for example, in Parson's theory of the ring electron; it would also follow from the law connecting electrostatic and magnetic force which I suggested some time ago.²⁶

If want of symmetry in the distribution of electrons is essential for paramagnetism, we can understand why it is confined to elements such as those we are considering, where the arrangement of the electrons in the inside of the atom may change, not merely from element to element, but even in a particular element under different external conditions. Outside such a group of elements the arrangement of the inner electrons does not change from element to element, it is very stable, and thus has probably a high degree of symmetry. It would, from this point of view, be interesting to test the magnetic qualities of compounds like CrF_6 and MnF_7 , in which the readjustment of the inner electrons has not taken place.

The researches of G. Wiedemann, Quincke, Townsend, Pascal, Weiss, Kamerlingh Onnes and others on the relation between magnetic properties and chemical composition have brought to light a great number of very striking phenomena, which are very diverse and in some cases anomalous, their very diversity, however, renders them all the more suggestive.

For salts in solution, and the same seems to be true for salts in the dry state, especially if these contain water of crystallization, the value of k , the coefficient of magnetization, *i.e.*, the quotient of the induced magnetization by the magnetic force, depends upon whether the metal is in the *-ous* or *-ic* state, but does not depend upon the acid radicle with which it is combined. Thus if a solution contains a definite amount of ferric iron the value of k will be determinate, it does not matter whether the dissolved salt is ferric chloride, ferric sulphate or ferric nitrate. The same is

²⁶ *Phil. Mag.*, 37, p. 419.

true for the ferrous salts; again the value of k depends only on the quantity of ferrous iron, but the value of k for the same weight of iron will depend upon whether the iron is in the ferrous or ferric state. Thus if W is the weight of iron in a cubic centimetre—

$$10^7 k = 2660W - 7.7 \text{ for ferric salts.}$$

$$10^7 k = 2060W - 7.7 \text{ for ferrous salts.}$$

In such salts as ferrocyanide of potassium where the iron appears on the negatively electrified part of the molecule, thus $\text{K}_4^+ (\text{FeCN}_6)^-$, the compound is not paramagnetic at all, but slightly diamagnetic. The ferricyanide $\text{K}_3 (\text{FeCN}_6)$ is slightly paramagnetic, although the paramagnetism is very small in comparison with that of the ferrous or ferric salts. Similar results are shown by the magnetic metals Cr, Mn, Ni, Co. Copper itself is diamagnetic as are also the cuprous salts; the cupric salts, however, are magnetic. The oxides and sulphides of the magnetic elements show large variations in their magnetic properties, thus magnetite Fe_3O_4 , which is regarded as a compound of FeO and Fe_2O_3 , is much more magnetic than either of them, and a similar statement is true for the corresponding sulphur compounds. Again variation in the temperature may produce great changes in the magnetic properties of an element, thus four types of iron, α , β , γ , δ , have been detected by Osmond and other workers; these pass from one into the other when the temperature passes through definite stages, and each of these types of iron has characteristic magnetic properties. In discussing the meaning of these results we must remember that on the view that paramagnetic properties are due to the setting of magnets, or their equivalents, under the action of a magnetic force; the magnetization, unless the field is intense enough to produce saturation (a state of things which is not attained with solutions), will depend upon two quite distinct things: (a) The resultant of the moments of the magnets; (b) the restoring force which tends to keep the magnets in the position of equilibrium. A substance may have a small coefficient of magnetization either because it contains few magnets or because the restoring force is very great, so that a given external field produces but a small displacement of the magnets. Thus the difference between the coefficients of magnetization of ferrous and ferric iron may be due either to the difference of the magnetic

moments of the magnets in the atom in the two states or to a difference in the restoring force. If it is due to a difference in the magnetic moments the intensity of magnetization when the ferrous iron is saturated will not be the same as when the ferric iron is saturated, whereas if it is due entirely to the difference in the restoring force the saturation magnetization will be the same in the two cases. We can distinguish between these effects by Weiss' Theory of Magnetons as the number of magnetons is proportional to the magnetic moment. The result of the application of this theory is that the number of magnetons per atom of iron in ferrous sulphate is 27, in ferric it is 29. As the coefficient of magnetization differs more widely than these numbers, it follows that the restoring forces must be different in the ferrous and ferric salts. In the iron in potassium ferricyanide Weiss finds that there are only ten magnetons. The difference between the number of magnetons in the trivalent and divalent condition is more pronounced in chromium and cobalt than it is for iron, thus for trivalent chromium the number of magnetons is 19, for divalent 25, in trivalent cobalt the number is 17, in divalent between 24 and 26; thus in both these metals the number of magnetons in the trivalent condition is greater than in the divalent, whereas in iron the trivalent form is slightly richer in magnetons than the divalent. A very striking case of the variation of the number of magnetons with chemical composition is that of the oxides and sulphides of vanadium. Wedekind and Horst ²⁷ give the following values for k the coefficient of magnetization and n the number of magnetons in various compounds of vanadium.

	$k \times 10^6$	n
VO	50.06	13.9
V ₂ O ₃	13.88	10.92
VO ₂	3.73	4.19
V ₂ O ₅	0.86	2.99
VS	7.22	5.86
V ₂ S ₃	8.95	10.00
V ₂ S ₅	12.55	11.90
VOC1	27.16	13.18
VN	4.13	3.92

²⁷ *Chem. Berick.*, 45, 263 (1911).

Thus the effect of oxygen is of the opposite character to that of sulphur, an increase in the oxygen content decreases, while an increase in sulphur content increases the number of magnetons.

Let us now proceed to see how the magnetic properties of the salts of the magnetic metals are consistent with the following assumptions:

1. That the paramagnetism of these substances arises from the atoms of the paramagnetic element. Fe. Cr. Mn. . . .

2. That the magnetic properties of these atoms arise from a want of symmetry in the distribution of the electrons in the inner layers.

3. That the distribution of these electrons and therefore the symmetry of their arrangement can be affected by intense electric forces arising from atoms with their electrons in the neighbourhood of the atom of the magnetic element, and that such forces may also affect the restoring force of the electrons in the atom, *i.e.*, the force with which the system of electrons resists any displacement from their position of equilibrium.

We shall take in the first place the very large diminution in magnetic properties which takes place when the atom of the magnetic element is a constituent of a complex salt such as $K_4(FeCN_6)$ ferrocyanide of potassium. We may point out that this diminution may take place when the magnetic element occurs in a complex with the positive charge and not merely when as in $K_4(FeCN_6)$; the iron is a member of the negatively electrified group. Thus Feytis²⁸ has shown that the following cobalt salts are diamagnetic— $(Co(NH_3)_6)Cl_3$, $(Co(N_4)_5Cl)Cl_2$, $(Co(N_4)_4Cl_2)Cl$ and $(Co(NH_3)_5H_2O)Cl_3$; though in all of these the cobalt atom occurs in the positively electrified portion of the complex molecule.

What is the condition of the atom of the metal in a complex salt? Let us take potassium ferrocyanide as an example, for similar considerations will apply to all the complex salts. In potassium ferrocyanide the iron atom has lost two electrons and is surrounded by 6CN radicles, all of which are negatively electrified. Considerations of symmetry suggest that these negatively electrified radicles are at the corners of an octahedron and the iron atom at the centre. The cyanogen radicles are, using Werner's notation, in the first zone with the atom of iron and are much

²⁸ *Comptes Rendus*, 152, 708 (1911).

more closely attached to it than are the atoms of potassium which are in the outer zone. Thus by the close proximity of the negatively charged cyanogens, the atom of iron is exposed to an intense and very symmetrical field of force, and this would (1) give rise to a very strong restoring force; this, if there were no change in the magnetic moments, would until saturation is approached reduce the magnetization. (2) From its symmetry this field tends to make the arrangement of the electrons inside the iron atom more symmetrical and thus reduces the magnetic moment. Both effects occur, the magnetization at ordinary temperature is reduced so much that it is not able to overcome the diamagnetism which iron, like all systems containing electrons, possesses; the number of magnetons is, according to Weiss, reduced to ten, which is only about one-third of the number in an atom of ferric ion. Let us now consider simple salts either in solution or which contain water of crystallization. Since these are electrolytes, the negative constituents of the molecule, such as Cl , SO_4 , NO_3 , will not be in the inner zone with the iron or other magnetic molecule, but in the outer zone. Thus these negative constituents will exert but little influence on the iron atom, and thus its state and magnetic properties will be but little affected by the change of SO_4 for Cl_2 and so on. The molecules in the zone nearest to the iron atoms are water molecules; these are probably arranged symmetrically around the iron atom and it is also probable that there are six molecules of water in the inner zone. We may picture the atom of iron as at the centre of an octahedron with the water molecules at its corners. As far as the geometrical arrangements are concerned, they are very similar to those of the ferrocyanide with water molecules in place of negatively charged cyanogen radicles. As the water molecules are as a whole uncharged, while the cyanogen ones are negatively charged, we should have expected the field of force to be much stronger with the cyanogen atoms than with the water molecules, so that in the simple salt both the restoring force and the tendency to make the distribution of electrons symmetrical would be less than in the complex salt. Thus both the magnetization and the number of magnetons would be larger for the simple salt than for the complex one. In the salt where iron is trivalent, the iron atom will have lost three electrons; while in the divalent ones, it will only have lost two. Thus there

is a difference in the number of electrons in the atoms; this might of itself be supposed to affect the magnetization. In addition to this, since the charge on the trivalent atom of iron is greater than that on the divalent, its attraction on the water molecules will be greater, these will be drawn closer into the atom and will be more favourably situated for influencing the arrangement of the electrons in the atom of iron.

In the case of the oxides the conditions are more complicated, we should expect as a general result that in these compounds the closer the connection between the iron and the atoms with which it was combined the lower would be the magnetization and that anything which tended to loosen these bonds would increase the magnetization. A loosening of these bonds would, however, increase the chemical activity of the iron by rendering it easier for it to enter into other combinations, thus we should expect to find correlation between chemical activity and magnetization, a connection which is brought to light very clearly by the experiments of Pascal. From this point of view we can understand a remarkable result obtained long ago by G. Wiedemann, *viz.*, that the magnetic qualities of Fe_2O_3 were increased by mixing with it Al_2O_3 ; the substances are isomorphous and may combine and form a compound in which the iron is not so firmly bound to other atoms as in Fe_2O_3 .

(To be Continued.)

Soaring Flight of Gulls following a Steamer. E. H. HANKIN. (*Proc. Cambridge Phil. Soc.*, Vol. xxi, Part IV.)—When a steamer is moving dead into the wind there is an ascending current at the forward end and, strange to say, another at the stern close to the vessel, while perhaps from 10 to 50 yards farther astern there is a descending current. The existence of these two currents astern has been demonstrated by letting out a length of cotton thread. This rose from the vessel at an angle of about 60° with the horizontal, stretched out parallel to the sea farther away, and still farther off descended. The soaring gulls use the descending current astern by preference. If one gets into the adjacent ascending current it has to resort to flapping to win its way into the descending stream. Gliding may take place also in the ascending windward current, but here gain of height is less rapid than in the corresponding current astern. "That a gull should soar in an apparently descending current is, perhaps, not more surprising than that a vulture should glide with gain of height in an apparently horizontal wind."

G. F. S.

The Variation of Metallic Conductivity with Electrostatic Charge. F. WENNER, NYNIA L. FORMAN, and A. L. LINDBERG. (*Phys. Rev.*, December, 1922.)—H. A. Perkins in 1921 said "A simple conception of metallic conduction based upon moving electrons seemed to justify the assumption that a negative charge should increase the conductivity of a circuit, and a positive charge should decrease it." He devised a method, performed the experiment and obtained results in confirmation of his hypothesis. The three investigators in the bureau have performed a similar crucial experiment and have obtained results discordant with those of Perkins. "If, therefore, the observations are reliable, we may conclude that when the potential of a practically straight, .08 mm.-diameter, copper wire, is charged from + 6000 volts to - 6000 volts, its resistance is changed, if at all, by not more than one part in 5 million, or not more than 2 per cent., of that reported for the original experiment."

A note adds that Professor Perkins has found the cause of his large result and will publish an account of a repetition of his experiment.
G. F. S.

Philadelphia-Pittsburgh Section of the New York-Chicago Cable. J. J. PILLOID. (*Bell System Tech. J.*, July, 1922.)—This line, more than 300 miles long, was designed to operate in conjunction with the Pittsburgh-Chicago cable and to fit in with other fundamental cable projects. In view of the topography of the country to be traversed and of the conditions of service, small-gage, quadded, lead-covered aerial cable was decided upon. Poles twenty-five feet long are used. The cable is strung from a steel suspension strand which is normally under a tension of 7000 pounds. The sheath is of lead-antimony alloy, one-eighth inch thick. "The wires are first wrapped with dry paper for insulation and twisted into pairs and then two pairs are twisted into what is called a quad." Nineteen quads of No. 16 A. W. G. and 120 quads of No. 19 A. W. G. pure copper conductors are in the main sections of the cable. Loading coils are sealed in iron pots mounted on poles. "The improvement, insofar as the attenuation losses are concerned, varies with the type of circuit and loading coils, but with one of the No. 19 A. W. G. circuits in this cable loaded with coils having an inductance of 0.175 henry located at 6000-foot intervals, the losses are only one-third as great as in a similar circuit without the coils."

Telephone repeaters which receive small currents, amplify them and send them on without distortion are used by the hundred in the new line. These are filament-grid-plate vacuum tubes.

On the mountains 5-ton tractors were employed to transport the cable reels which weighed half as much as the tractor. Even these failed to overcome the difficulties of certain places and the cables had to be dragged for long distances.
G. F. S.

ANIMAL LUMINESCENCE.*

BY

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MR. CHAIRMAN, Members of the Institute, Ladies and Gentlemen: I think everyone in this audience understands what we mean by luminescence, a light which is produced at a relatively low temperature—"cold light." The word is contrasted with incandescence, a light which always accompanies a high temperature—"hot light." In fact, we never have high temperature of liquid or solid bodies¹ without a production of light, no matter what the substance is, whereas at low temperatures, it is only under certain special conditions that light is produced. I doubt if many, however, realize how common luminescence is. I will review briefly the various types of luminescence.

If I should place my hand under a strong light, an electric lamp, the skin, and especially the finger-nails, would give off a light of their own. This light to which I refer is not a reflected light, but a light which is actually produced in the skin and nails. We cannot see it, however, under these conditions because the light reflected from the incandescent filament is so strong that its intensity overpowers the intrinsic light which would be produced. We can arrange matters, however, so that this intense reflected light is cut off from our view and only the luminescence emitted from our skin and nails is seen. We speak of this emitted light as fluorescence. The teeth, the hair, the eyes, in fact every tissue in the body will fluoresce under certain conditions, so that this phenomenon of fluorescence is a very wide-spread one, provided we use the proper means to bring it out.

Stokes devised a means of doing this. He placed the substance to be examined in a dark box with two windows at right angles to each other. One window was covered with blue glass which allows only blue light to pass through and the other was covered with yellow glass which allows no blue light to pass.

* Presented at the Stated Meeting of the Institute held Wednesday November 15, 1922.

¹ Perfectly transparent bodies give off no light at high temperatures.

If we look at a white light through the blue and yellow glass together we see nothing. All the rays are absorbed by such a combination. If we allow the white light, however, to pass into our dark box through the blue-screened window and strike the material to be examined, at the same time observing this material through the yellow-screened window, we observe that the material, for example our finger-nails, will appear luminous. This can only mean that some of the blue rays have been converted by the finger-nails into other wave-lengths, among them yellow wave-lengths, which can then pass the yellow observing screen. This experiment shows that fluorescence is a conversion of one kind of radiation into another kind which is actually emitted (not reflected) by the body in question. No luminosity would be observed in the box unless the substance were fluorescent with yellow light that could pass the screen.

Usually short wave-lengths are converted into longer fluorescent wave-lengths. The ultra-violet is converted into visible by a great many fluorescent substances. It is sometimes of interest to consider what would happen if we were transported to a totally different environment from our own. Suppose that we were placed, with the eyes we now possess, on a planet illuminated by ultra-violet light alone. One might think that total darkness would be our fate. On the contrary we should be able to see each other and practically all living things (both plants and animals) as well as many objects in the mineral world, because of this fluorescent light.

It is possible to reproduce such conditions in the laboratory by use of a strong source of ultra-violet such as the mercury arc and Woods' ultra-violet filter, which absorbs the visible and allows ultra-violet wave-lengths of about $366\mu\mu$ to pass. As I will show you, silk, wool, bone, tendon, cartilage, horn, coral, chitin, cellulose and a host of organic substances become fluorescent in the mercury ultra-violet. We do not see the ultra-violet light from the mercury lamp but we do see visible light from the fluorescent body.

If I turn off the current, the fluorescence will cease and it appears to stop instantly. In reality we find that the fluorescent light often² persists for a fraction of a second, perhaps only 0.001

² But not always. No one has been able to measure the persistence of fluorescence of solutions.

second, after the exciting light is stopped. Instruments, phosphoroscopes, have been devised for examining this persistence of very brief duration, but we have not the time to consider these here.

If the fluorescent light does persist we call it phosphorescence and many impure sulphides (Ca, Ba, Sr, Zn) will give off light for hours after they have been exposed to previous radiation. Fluorescence and phosphorescence are essentially the same phenomenon, differentiated as they are by persistence of luminescence, whose observation we may make as short as our measuring instruments will allow.

I should, perhaps, emphasize strongly at this point that animal light production is not a fluorescence or phosphorescence in any sense, despite the fact that we often describe it as a "phosphorescence," a use of the word in quite another sense from its strict physical implication.

There are other kinds of luminescence, but many of them are too faint to demonstrate to a large audience. If we take two lumps of sugar and rub them together, or if we take sugar crystals and crush them, a light will appear, but that light is so faint you will have to experiment for yourselves to see it. This kind of light we speak of as a triboluminescence, a light due to fracture or crushing of the crystallized material. It is well shown by shaking crystals of uranium nitrate in a tube. Every time the crystals hit each other there will be a little flash of light produced, similar to that observed with sugar but much brighter.

If we take a piece of adhesive or electrician's tape and strip off the tape rapidly, you will find that at the moment it leaves the reel there will appear a faint luminescence. This may be an electric discharge or it may be a form of triboluminescence. I do not know what causes this luminescence but suggest that it may be due to the rubbing together of some minute crystals on the tape.

The last time I lectured on "cold light" some one told me that if you take a Nabisco wafer with a wintergreen flavor and break it in half, there will be a flash of light at the moment the wafer is broken. I wished to try the experiment and on going to a grocery store to purchase my experimental material, the salesman informed me there was no such thing as a Nabisco wafer with a wintergreen flavor. You may draw your own conclusions but I regret that I cannot show you the experiment. However, if you have an opportunity, you might try it yourselves.

If we take a saturated solution of common salt and add it to some alcohol or hydrochloric acid, the salt will crystallize very rapidly, and accompanying this crystallization will be the appearance of light. This is known as *crystalloluminescence*, and a great many other substances besides NaCl show luminescence during rapid crystallization.

If we take pyrogalllic acid, such as is used in photography for developing purposes, adding to it some hydrogen peroxide and then a little potato juice, the mixture will give a luminescence. This same luminescence is obtained if we substitute various kinds of animal blood for the potato juice. The blood and the potato juice contain oxidizers which transfer the oxygen of H_2O_2 to the pyrogallol which is oxidized with the accompanying emission of light. We have a luminescence produced by a very definite chemical reaction and speak of it as a *chemiluminescence*. The glowing of white phosphorous in the air is a similar luminescence. Oxygen is necessary for its production and as this is very generally the case we may speak of *oxyluminescences*. Although the flame of a candle or oil lamp requires oxygen we have here no *oxyluminescence*, but *oxyincandescence*, the heat of combustion of tallow or oil raising the temperature of carbon particles to *incandescence*.

Most of you have seen the phosphorescence of damp wood at night, or fox fire. That is due entirely to the presence of a fungus in the wood. Perhaps you have seen dead fish or meat in refrigerators, glowing in the dark. This is due entirely to bacteria living on the fish or meat. These bacteria can be raised artificially on the proper culture medium, and we can transfer them from one dish to another, thus keeping the colonies alive indefinitely. They give off their light continuously day and night. Bacteria and fungi are classified as plants, and, although the title of my lecture is "*Animal Luminescence*," in reality the plants can produce light as well, so that we might more correctly say, "*Living Luminescence*," or "*Living Light*."

Everyone has seen the phosphorescence of the sea. To the old observers this was rather a mystery, but we now know that all luminescence of the sea is due to one or another kind of small living creature, microscopic or macroscopic in size, mostly microscopic, however. I will now show you by lantern slides some of the organisms which are responsible for this light and point out the principles of living luminescence which they demonstrate.

The luminous animals of the sea may be unicellular or multicellular, simple or complex, but they all agree among themselves and differ from the plants which produce light, the bacteria and fungi, in that they must be stimulated to luminesce. You have no doubt noticed that phosphorescence of the sea is only apparent at the prow or stern of a ship where the water is violently agitated. Agitation serves as a stimulus to the minute creatures in it. Even the fire-fly gives off light on stimulation only, but in this case the stimulation is not mechanical, but nervous, arising in the nerve cells of the animal, just as voluntary contraction of our own muscles comes from nervous stimuli arising in the central nervous system.

The only exception to this rule is found among certain fish. I have said that dead fish very often become luminescent at night, which is due to luminous bacteria growing on them, but living fish may also produce light as well, and that is due to luminous organs in the fish. Certain forms which live in the East Indies, in one particular group of islands, the Banda Islands, have a large luminous organ under the eye, about one-fifth the length of the fish itself. This fish, *Photoblepharon*, is rather unique among animals in that the luminous organ produces its light continuously day and night and does not have to be stimulated to luminesce, but as the fish swim through the water they are constantly flashing, turning the light on and off so that they present a truly interesting picture. This is due to a sort of third "eyelid," a fold of black pigmented skin which can be drawn up over the luminous organ, thus shutting off the light.

When we study *Photoblepharon* carefully we find that the organ is made up of a mass of living bacteria. These bacteria will not live on ordinary culture media, and the fish is never found without them so that we have a true symbiotic relationship, and a mode of light production quite different from other forms. As the light of *Photoblepharon* is really due to luminous bacteria which belong in the plant kingdom, perhaps we need not regard it as an exception to the general rule that animal light appears only upon stimulation of the luminous tissue.

Other fish and certain kinds of shrimp and squid possess a row of luminous organs along the sides of the body which look like the port holes of a ship at night. In them a luminous substance is manufactured by the fish or shrimp or squid which gives

off the luminescence. There are no luminous bacteria in these organs. They often possess a complicated lantern-like structure for directing a beam of light. If we study their microscopic structure we find a picture something like this: A large amount of clear transparent tissue which is shaped like a lens to direct the light; a group of cells, called photogenic cells, in which the light is produced; a layer of cells below the photogenic cells which serve as a reflector; outside of and surrounding most of the organ another layer of cells containing a black pigment which form a screen and protect the tissues of the animal from its own light. Apparently even the light which the animals produce is injurious to them and they must have some way of protecting themselves. These organs were formerly supposed to be eyes, before it was known that they produced light.

I can only briefly mention other light-producing groups of animals—molluscs, beetles, flies, centipedes, crustaceans, brittle stars, earth-worms and marine worms, comb-jellies, jelly-fish, sea-pens, hydroids and the host of microscopic forms. Each group presents an interesting structural study, ably described by Dahlgren in the JOURNAL OF THE FRANKLIN INSTITUTE.

Those forms are most favorable for chemical study, which secrete a luminous material outside of the body (extracellular luminescence) as contrasted with those that produce light within the photogenic cells themselves (intracellular luminescence). One small creature, *Cypridina*, a crustacean about one-eighth of an inch long, has proven unusually good for chemical investigation and I will point out some of the discoveries which have been made on this material.

Our chemical knowledge has advanced in four important steps. The first step was made by Robert Boyle, in 1667, who showed that bioluminescence is always dependent on oxygen. He placed a small piece of phosphorescent wood in his air-pump and found that as he removed the air the luminescence disappeared, only to reappear again when air was readmitted. Of course at that time he did not know that the oxygen of the air was responsible, but I think we can credit him with the discovery that oxygen is necessary for luminescence.

The next step was the determination that almost any luminescent tissue could be dried, and, if dried rapidly, preserved unchanged for a long time. If, at any later time, moisture is added,

the light would appear. This was first tried on jelly-fish by an Italian, Spallanzani, in 1794.

The third important step was made by a Frenchman, Dubois, in 1865. Dubois found that in a mollusc, *Pholas*, there are really two substances necessary for light production, in addition to the oxygen and water already mentioned. One, which he called luciferin, is oxidized in the presence of the second, called luciferase, an enzyme. Enzymes are of the same nature, as you know, as the catalysts. These two substances can be separated from each other by marked differences in properties. The one which oxidizes with the production of light, luciferin, is not destroyed on boiling, so that if we wish to obtain a solution of luciferin we will make a hot water extract of the luminous animal. The hot water will destroy the luciferase, which has the properties of enzymes in general, among them destruction on boiling. If we wish to obtain the luciferase in solution we make a cold water extract of the luminous animal. Such an extract will contain both luciferin and luciferase and will luminesce for quite a while, but in time the light will disappear and that is, of course, because the luciferin is being continuously oxidized and is finally used up. The luciferase, being an enzyme, is not used up and remains in the cold water extract.

As I will show you, it is possible to prepare two tubes, one containing luciferin solution, and quite dark, the other containing luciferase solution and also dark, which will give a bright luminescence if mixed. The glow becomes fainter and fainter and finally disappears when all the luciferin has been oxidized.

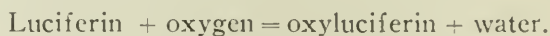
The fourth step is our realization that the oxidation product of luciferin, which I have called oxyluciferin, can be reduced to luciferin again. I had frequently observed that solutions of perfectly dark luciferase, which, from mode of preparation must contain also oxyluciferin, were capable of giving off more light after standing for a few days. In 1918, I found that this was due to reduction of the oxyluciferin by bacteria,³ whose strong reducing action is well known, growing in the solution. Many means of reduction of oxyluciferin are possible, involving the use of well-known reducing agents.

No one knows the exact chemical composition of these two photogenic substances. Luciferin has many properties in com-

³ Not luminous bacteria but other kinds.

mon with the proteoses and peptones and may be considered intermediate between these two groups. Luciferase has the properties of an albumin and is an albumin, or so closely bound with albumin, that the two cannot be separated. All those who have worked with enzymes know the difficulties of their purification.

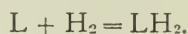
Although we cannot write a structural formula for luciferin I will point out what I believe is the essential change taking place during reduction and oxidation, namely, a hydrogenation and dehydrogenation, thus :



or, symbolically,



When oxyluciferin is reduced under the influence of reducing agents we have—



The luciferin is thus regenerated. I find that reduction may be brought about by hydrogen sulphide or other sulphides, by the action of acids or alkalies on metals, whereby nascent hydrogen is produced, by palladium and sodium hypophosphite, and by reducing enzymes. My usual procedure was to add the reducing agents to a solution of oxyluciferin made by thoroughly boiling an extract of *Cypridina* in order to destroy the luciferase and oxidize all the luciferin to oxyluciferin. After allowing the oxyluciferin solution to stand for some time in contact with reducing agent, the presence of luciferin could be detected by adding luciferase solution and noting if any light occurred. If anyone doubts that reduction of the oxyluciferin is really the phenomenon observed in these experiments, I think the following observations are sufficient to prove conclusively the reality of reduction.

It is a well-known fact that reduction occurs at the cathode and oxidation at the anode when an electric current is sent through a solution. If, between platinum electrodes, a current is sent through an extract of *Cypridina* containing luciferase and oxyluciferin and some NaCl, to make it a good conductor, a beautiful luminescence appears over the surface of the cathode, none over the anode. With *n* NaCl, the luminescence is just visible at 1.8 volts across the electrodes and is marked at 2 volts. This is about

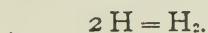
the potential at which hydrogen first appears in an n NaCl solution and is very slowly liberated as bubbles from the electrode.

The explanation of this experiment is as follows: Nascent hydrogen is liberated through decomposition of water by the Na set free at the cathode.



The nascent hydrogen, H, reduces the oxyluciferin to luciferin, which then oxidizes with luminescence in contact with luciferase and oxygen, also present in the solution. Thus we have a layer of luciferin formed in immediate contact with the electrode and just beyond this, the oxidation of the luciferin to oxyluciferin with luminescence. By the use of oxyluciferin solution containing luciferase and oxygen we have a means of immediately determining that reduction of the oxyluciferin has occurred, which is more convenient and rapid than former methods in which I first reduced an oxyluciferin solution in absence of oxygen and then mixed it with luciferase solution containing oxygen. The present method is especially applicable to the study of reductions at the surfaces of solids and gives us an interesting insight, as we shall see later, into the action of heterogeneous catalysts.

Not only may the luminescence under the above conditions serve as an indicator of reduction of oxyluciferin, but conversely the luminescence may serve as an indicator of nascent or atomic hydrogen. Hydrogen from a cylinder will give no luminescence whatever if bubbled in a fine stream or shaken (so as to break it up into very minute bubbles) with oxyluciferin-luciferase-oxygen solution. Only if the hydrogen is liberated in the oxyluciferin-luciferase-oxygen solution so that the hydrogen possesses its "active" qualities will luminescence occur. The "active" qualities persist only within very small distances from the surface of separation, as can be easily demonstrated by this luminescent reaction. The "active" hydrogen is no doubt atomic hydrogen which changes rapidly in the sense of the equation:



If oxyluciferin can be reduced at cathodes during electrolysis it should be possible to observe reduction of oxyluciferin when present in a fluid serving as the electrolyte of a voltaic cell, in which two dissimilar metals are placed. It should also be possible to

observe reduction of oxyluciferin at the surface of metals capable of liberating hydrogen from water. Both possibilities can be realized.

I find that Mg, Al, Mn, Zn, and Cd, placed in oxyluciferin-luciferase-oxygen solution, luminesce over their fresh-cut surfaces. None of these metals liberate visible hydrogen from water at room temperature except Mg, but a thin film of atomic H must be formed over their surface, which is replaced as used in reducing oxyluciferin, for the luminescence may last for some time.

We are now in a position to describe the luminescent effects at galvanic couples formed in oxyluciferin-luciferase-oxygen solution plus NaCl to render the solution a conductor and electrolyte. As I have said, if a strip of Zn or Al or Cd is placed in such a solution the metals glow spontaneously. A piece of platinum placed in the solution does not glow, but if the Zn or Al or Cd is touched to the platinum, the platinum luminesces quite brightly, with greater intensity than the Zn or Al or Cd alone. At the same time the luminescence of the Zn or Al or Cd either fades or disappears. The platinum forms the cathode of the galvanic circuit at which reduction processes occur, the oxyluciferin is reduced to luciferin in immediate contact with the platinum and then is oxidized again with luminescence by the luciferase and oxygen layer next to it.

It is also possible to reduce oxyluciferin in presence of molecular hydrogen providing that a catalyst is present. As is well known, there are two groups of catalysts used in hydrogenation processes in the industries, namely, the Pt group and the Ni group.

Palladium and platinum are active examples of these. A palladinized or platinized surface, if saturated with hydrogen and then placed in oxyluciferin-luciferase-oxygen solution will glow beautifully. No luminescence appears if the Pd or Pt surface is first exposed to oxygen and then placed in the above solution.

A continuous luminescence appears if hydrogen from a cylinder is bubbled through an oxyluciferin-luciferase solution which contains palladinized gauze or colloidal Pd or Pt. It is not necessary that the hydrogen be produced in the atomic or nascent condition in contact with the metal catalysts. Molecular hydrogen in contact with Pd or Pt is converted into the active state as is evidenced by the luminescence in the above-mentioned experiment.

We may, therefore, conclude that the reason palladium acts as a catalyst is because of its power to convert molecular into nascent atomic hydrogen.

It may perhaps be emphasized in passing that we have here a means of producing a luminescent lamp which would burn for an indefinite time,⁴ provided a slow stream of hydrogen and oxygen be supplied. A large palladinized surface would continually reduce oxyluciferin which would just as continually reoxidize with luminescence in presence of luciferase and oxygen. In actual practice the light produced in this way is too weak for purposes of illumination. It is a mere scientific curiosity at the present time, but I believe the principle involved an important one. Suppose we could find a substance which produced a bright light during oxidation and which was readily reducible, as oxyluciferin is. The material could be used over and over again. It would be equivalent to burning oil in a lamp and then reducing the oxidation products of the oil, the CO_2 and H_2O to oil again. A procedure not possible in the case of oil, surely, but worth considering in connection with some chemiluminescent materials.

Let me recall again to your minds the distinction between the luminous bacteria and fungi which glow continuously day and night, and the animal organisms which glow only on stimulation. Most students of bioluminescence have supposed that luciferin is continually being formed from some simpler substance as it is oxidized with light production. We may quite logically believe that the bacteria and fungi oxidize luciferin in one part of the cell and reduce oxyluciferin in another, while the animal organisms oxidize luciferin during the flash and reduce it between flashes. Should this be true, and it is not proven as yet, living processes would present a marvel of economy quite at variance with the prodigality we are apt to associate with reproductive nature.

Another phase of this work in which I have been much interested recently is a determination of the factors which control the intensity of the light. A student of mine, Dr. W. R. Amberson, has been working on this problem and has succeeded in measuring the light intensity in a test tube of solution whose luminescence gradually fades. What we wish to determine is the curve of this luminescence intensity against time, or the decay curve, to see

⁴Unless secondary reactions appear which interfere with oxidation and reduction.

upon what factors intensity depends. The problem is a difficult one but he has solved it by means of a photographic method. He has photographed the light on a moving picture film wrapped on the drum of an ordinary kymograph such as is used in physiology laboratories. The container for the luminescent mixture is a tube of glass, covered with black paint and adjusted very near the drum. On one side is a small slit, through which the light produced can shine directly on the film. A stirring device and thermometer are also placed in the tube. With two such tubes it is possible to take two records at the same time on the same moving picture film. A calibration record must also be placed on the same film. If we take records in this way during revolution of the drum, we get a streak of blackening on development which gradually fades out as the film revolves and the luminescence becomes less intense. The calibration exposures are made in order to determine how much blackening a given intensity of light will produce on the film. They are obtained by allowing the same luminescence to pass through neutral filters of known absorption before striking the film and must be impressed after the moving record is taken.

Doctor Amberson has studied the effect of changing the (1) concentration of luciferin, (2) concentration of luciferase, and (3) temperature. Oxygen is always present in such high concentration that it does not affect the light intensity even though its concentration may vary somewhat during the course of the reaction. The curves obtained are always straight lines if we plot log intensity of luminescence against time. This is just the result we should expect, if the oxidation of luciferin represents a monomolecular reaction, whose reaction velocity determines light intensity, and is presented as proof that reaction velocity does determine light intensity, within, of course, certain limits.

The luminescence intensity (reaction velocity) is about proportional to the concentration of luciferase and to the concentration of luciferin (presumably) and doubles or trebles for a rise of temperature of 10° C. There is an interesting initial flash of greater intensity than we should predict from theory lasting one or two seconds. This flash suggests conditions obtaining in a heterogeneous system but I cannot take the time to discuss this matter now.

You may be interested in some work that has been done upon the physical nature of animal light, that is largely due to Ives and Coblentz. In a photograph showing the spectrum of the light of a fire-fly, compared with the helium spectrum and the carbon incandescent light spectrum, the fire-fly spectrum occupies only a small region centred in the yellow and is not crossed by any dark or light bands or lines. You have probably noticed that some fire-flies have different luminescent color from others. Some flash with a deeper red than others. These differences in the color of the light are due to real spectral differences in the lights themselves and are not subjective illusions of our own eyes.

Some fire-flies actually possess lights of two different colors on different parts of the body and it is true that the spectra of all luminescent organisms differ somewhat. The form that I have been working with, *Cypridina*, is very different from the fire-fly. It has a very blue light but its spectrum extends over quite a range of wave-lengths. There are no infra-red and no ultra-violet rays emitted by luminous animals. There are also no penetrating radiations of any kind.

Since all radiation is in the visible, the luminous efficiency is very high, whereas in an incandescent lamp, so much of the radiation is in the infra-red that the luminous efficiency is very low. We must always remember, however, that animal light is in no way different from any other kind of light. It can be refracted and reflected and polarized, will affect the photographic plate, cause decomposition of CO_2 in presence of chlorophyll and show all the phenomena which ordinary light of the same wave-lengths exhibits.

Finally we may inquire as to the actual intensity of these lights. Everyone knows that the actual candlepower of the fire-fly is very low indeed. It is a little difficult to measure accurately, but Coblentz estimates that the flash of the fire-fly might vary from $1/400$ to $1/250$, and Pickering states that it has an intensity of about $1/250$ candlepower, so that these candlepowers are not to be compared with the light we use to-day for illumination. However, the important fact is not the candlepower but the candlepower per area that gives off the light; what we call the intrinsic brilliancy of the light. Ives has measured it, in the case of the glowworm, which is easier to measure, as perhaps you know, the flash of the glowworm lasts a great deal longer than that of the fire-fly. He

found that the luminescence possessed an intrinsic brilliancy of .0144 lumen per square centimetre. From that we can calculate how large an area of this intrinsic brilliancy on the ceiling would be necessary to illuminate a table underneath. To properly illuminate this table, if the table is a metre high and the whole room three metres high, it was found that a disc of light on the ceiling must be two metres in diameter. If such were the case, we could then obtain a light on the table that would be ample for reading or writing or drawing. If it is possible to copy the fire-flies process you see it may not be entirely out of the question to use such light for illuminating purposes. The modern tendency of indirect lighting is to use a diffused light rather than the highly concentrated lights of enormous intrinsic brilliancy. I think it will be quite possible to reproduce the process of luminescence of living things, but whether it will be feasible to do so cheaply, commercially, is of course a question which only time can decide.

New Experiments on Photophoresis. J. MATTAUCH. (*Physikal. Zeit.*, Oct. 15, 1922.)—This name was given by Ehrenhaft to the translatory effect exerted by a concentrated beam of light upon tiny particles with electrical charges which by means of such charges are made to hover suspended between the two plates of a condenser. The particle may be moved forward in the direction along which the light passes (light-positive) or backward against the beam (light-negative). According to Maxwell's theory there would be a pressure produced by light only in the forward direction. Laski and Zerner have, however, developed a theory of photophoresis according to which the direction of the motion depends upon the location of the point of maximum temperature in the hovering sphere.

Most of the experiments were conducted with particles of selenium which has at least two modifications reproducible at will. The first variety was red and the time required for them to fall through a given distance did not change as time went on. This indicates that there was little or no evaporation. All the spheres having a radius greater than 17×10^{-6} cm. were light-positive. Those with radii from this down to 10×10^{-6} cm. were light-negative. With smaller spheres no effect was discernible. At the other end of the scale of sizes the light-positive effect went on increasing as the radius grew.

With the second, the white, form of selenium, the time of fall varies in such a manner as to show that the substance evaporates. All spheres independent of their size were light-negative, but there was a maximum effect at a certain radius. There are similarly two modifications of sulphur which in general comport themselves like the red and the white varieties of selenium so far as photophoresis is concerned.

G. F. S.

CHEMISTRY OF THE ACID FIXING BATH.*

BY

S. E. SHEPPARD, FELIX A. ELLIOTT and S. S. SWEET.

THE acid fixing bath, now so general for both negative and positive processes, represents an interesting compromise between certain practical requirements, and limiting physico-chemical equilibrium conditions. This may perhaps be best exhibited by first tabulating the constituents and their respective functions, and then discussing in some detail how the exercise of these functions is governed by specific physico-chemical factors.

TABLE I.

General Composition of Acid Fixing Bath.

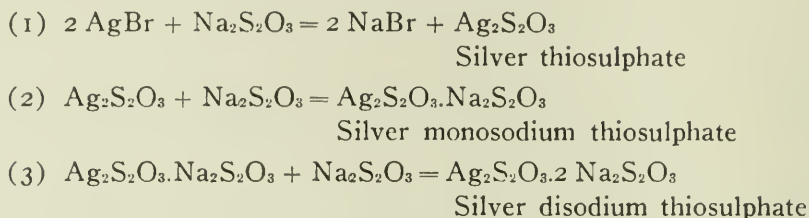
No.	Constituent.	Function.	Formula, etc.
1	Hypo	Fixing agent proper, dissolving silver halide	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
2	Acid	Clearing agent, promotes swelling and increases speed of fixing, reduces stain and coloration, and is necessary to regulate hardening agent (4)	H_2SO_3 (sulphurous) or organic acid (see later)
3	Sulphite	Protects hypo against decomposition by acid. Antioxidant and anti-stain	Na_2SO_3 $\text{Na}_2\text{S}_2\text{O}_5$ (meta-bisulphite)
4	Alum	Hardens gelatin, preventing frilling, softening, etc.	Potash alum K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$ Chrome alum K_2SO_4 , $\text{Cr}_2(\text{SO}_4)_3$
5	Water	Solvent	H_2O

Considering now the physical chemistry of each agent and function, respectively: With regard to "hypo" and fixation proper there is not much to note. The solution of the residual silver halide after development depends primarily upon the for-

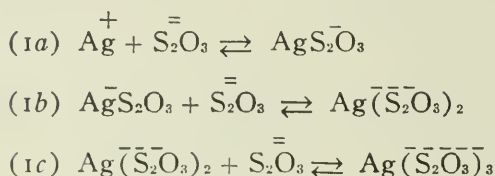
* Communicated by Dr. C. E. K. Mees, Director of Research Laboratory and Associate Editor of this JOURNAL. Published as communication No. 175 from the Research Laboratory of the Eastman Kodak Company.

mation of complex double salts. It should be noted that many double salts, or molecular addition compounds, may exist in the solid state, which give practically no evidence of combination in solution. The alums approach this condition. In general, there exists a wide range of such bodies, from such in which the dissociation into the simpler component molecules and ions is almost complete, to such giving very stable complex ions. The Abegg-Bödländer theory of electro-affinity regards such complex ions as formed by the union of simple ions with neutral molecules. Such complex ions may be regarded as transitional to colloids, particles in which we have a great number of neutral molecules stabilized by the adsorption of simple ions.

In terms of the double salt nomenclature, the solution of a silver halide, say AgBr, by thiosulphate, is represented by the equations:



or in terms of the reacting ions, and indicating the reversibility of the reactions



For a given silver halide, the ultimate or basic condition for the efficiency of a fixing bath is the stability of the silver complex ion formed. Thus the stability of the complex $\text{Ag}\bar{\text{S}}_2\text{O}_3$ is measured by the value of the expression:

$$\frac{[\text{Ag}^+][\text{S}_2\text{O}_3^{=2-}]}{[\text{Ag}\bar{\text{S}}_2\text{O}_3]} = K$$

where the square brackets indicate concentrations. These "complexity constants" may be determined in various ways experimentally.¹ Further, from the form of the expression it will be seen

¹ Jacques, "Complex Ions," Longmans, Green and Company, London.

that K is proportional to the concentration of silver cations. Now this will be determined by the solubility product of the silver salt.

For $\text{Ag}^+ + \text{Hal}^- \rightleftharpoons \text{AgHal}$ we have in the presence of solid halide

$$\left[\text{Ag}^+\right] \left[\text{Hal}^-\right] = \text{const.} = \text{solubility product}$$

Hence, the *less* soluble the given salt is in water, the higher must be the stability of the complex ion formed to ensure complete solution. Thus potassium or sodium cyanide is necessary to dissolve silver sulphide, Ag_2S , the least soluble of silver compounds, and it will be seen from the following table that the complex silver cyanidion is the most stable:

TABLE II.

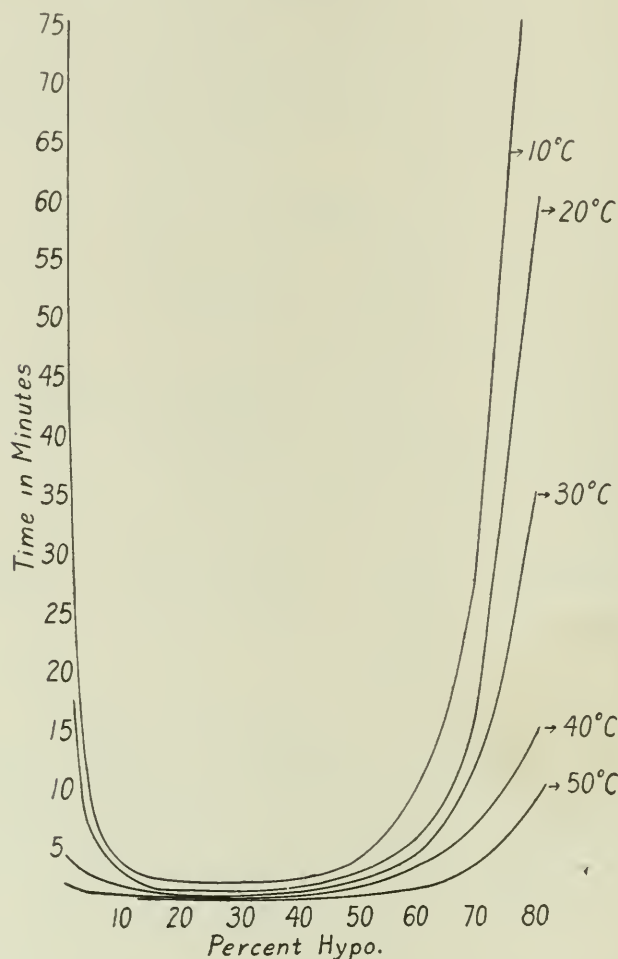
Formula of Silver Complex Ion.	Condition Electric.	Conc'n Limit of Free Anion.	K .
$\text{Ag}(\overline{\text{S}_2\text{O}_3})_2$	anion	below .1 N	$.98 \times 10^{11}$
$\text{Ag}(\overline{\text{S}_2\text{O}_3})_3$	anion	above .5 N	3.45×10^{13}
$\text{Ag}(\overline{\text{CN}})_2$	anion	under .05 N	$.11 \times 10^{22}$
Ag_2I_4 to AgI_2	anion	indefinite	7.7×10^{13}
$\text{Ag}(\overline{\text{CNS}})_2$	anion	below .2 N	6×10^9
$\text{Ag}(\overline{\text{CNS}})_3$	anion	above .3 N	1.5×10^9
$\text{Ag}(\overline{\text{NH}_3})_2^+$	cation		$.15 \times 10^5$

These are the fundamental equilibrium values determining the ultimate efficiency and economy of a fixing solution. The rate of fixation is, however, greatly affected by quite other considerations than these conditions of chemical equilibrium. It was shown by Sheppard and Mees² that for relatively dilute solutions of "hypo," up to 5 per cent. the rate of fixation is directly proportional to the concentration of the "hypo," and gives, over a considerable range, a linear function of the time. Further, it was shown that the speed of fixation depends greatly upon stirring. It was concluded from these results that the speed of fixation is primarily determined by the rate of interchange of the soluble components between the film and the solution, and principally by the diffusion out of the complex ion.

² "Investigations," p. 113 *et seq.*

These experiments were made for concentrations lower than those used in practice, and bear on the *rate*, rather than the total time of fixation, which chiefly concerns the photographer. A valuable series of investigations on the integral time of fixation—or better, the semi-total time—was described by Welborne Piper.³ As a criterion for the “time of disappearance” he used a streak

FIG. 1.



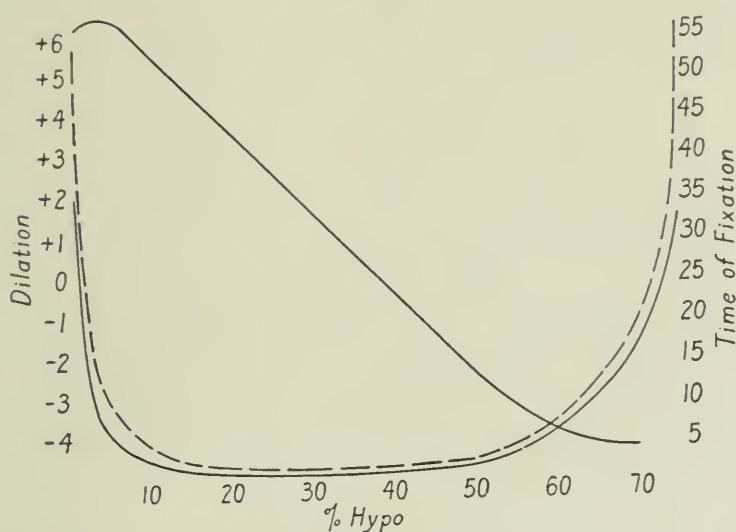
of hypo solution made across the plate before immersion, the “time of fixation” being the time for this to vanish. He found that an optimum concentration of “hypo” existed, giving the least time of fixation, at ordinary temperatures, between 30 and 40 per cent. Fig. 1 shows curves for experiments made by us on Seed process plates kept in motion during fixation.

In a general way the data confirm Piper's results. They show

³ B. J., p. 59, 1913.

that the influence of temperature is a pronounced function of the concentration. Increase of temperature has evidently a double influence, increasing the rate of diffusion, and also increasing the swelling of the gelatin. The values at 40° and 50° C. for low concentrations of hypo indicate that swelling is passing here into solution. The existence of an optimum concentration (for least time of fixation) appears to be due to the point of balance between increase of diffusion velocity with concentration, and decrease of swelling of gelatin with concentration of the saline hypo solution.

FIG. 2.



Outside curves show time of fixation, inside (linear) curve swelling compared with water.

STRATO-CHEMICAL FACTORS.

When a reaction can proceed with different velocities, and often to different apparent equilibria at different depths in a system little susceptible of internal mixing by convection, we encounter a variety of phenomena conveniently termed "strato-chemical." From the evident importance of the osmotic interchange between outer solution and the gelatin film in fixation we should expect strato-chemical factors to be of importance. Thus the integral time of fixation is mainly determined by the reaction-time of the lowest layer, adjacent to the support. Not only does the thickness of the film play a great part, but the position of the plate, particularly at rest. Thus we find a great difference in time of fixation between plates fixed at rest, in a horizontal position, according as the gelatin emulsion side is upmost or down-

most. In fact, a plate fixing at rest, but with gravity assisting the removal of the reaction-products, does not lag far behind one kept in movement. It seems probable that the gravitational down-flow of the heavier complex compounds tends to produce a local current at the plate surface. Two examples will suffice to illustrate this.

TABLE III.

Plate.	Per cent. Hypo.	Time of Fixation—Secs.	Position.	Ratio.
Seed 23	16	523.0	face up	2.3
	16	227.0	face down	
	16	183.0	in motion	
	32	126.0	face up	1.62
	32	139.3	face down	
	32	109.0	in motion	

ACID IN FIXING BATH.

The acid fixing bath was introduced by A. Lainer in 1889, with the object of combining the acid clearing bath frequently used after development with alkaline organic developers to remove yellow oxidation stain. Using dilute solutions of various acids, as sulphuric, formic, tartaric, acetic and citric, he found that milkiness due to precipitation of sulphur could be overcome by combining the acid first with sodium bisulphite solution and adding this to the thiosulphate.⁴ Under these conditions, provided the acid is not too strong, the solution remains clear and does not deposit sulphur. Instead of tartaric or citric acids, metabisulphite may be used.

Lainer's theory of the acid fixing bath based on preferential decomposition of the sulphite, and assumed formation of acid salts does not appear adequate. A more satisfactory explanation is derived from certain independent investigations on the physical chemistry of the decomposition of thiosulphates by acids. H. Landolt,⁵ in a paper on the "Time of Existence of Thiosulphuric Acid in Aqueous Solutions," reached the following conclusions: (i) The nature of the acid employed does not affect the decomposition; (ii) the time of stability is independent of excess of

⁴ *Phot. Corresp.*, 1889.

⁵ *Ber.*, 16, 2958, 1883.

thiosulphate or of acid; (iii) it is also independent of the absolute volume of solution; (iv) the decomposition starts sooner with increased temperature, but the temperature coefficient falls with rising temperature. It is facilitated by dilution.

Landolt considered that the "life-period" of thiosulphuric acid was measured by the interval between the addition of an acid solution to thiosulphate and the first appearance of a sulphur cloud or opalescence.

This induction-period was made the subject of an extensive investigation by H. von Oettingen.⁶

Considering that all the reactions were between ions, he supposed that the actual reaction was between the thiosulphate ion and the hydrogen ion from the acid, according to the equation



According to this, neither the sodium ion nor the acid anion take part in the reaction, which explains why the nature of the acid does not affect the decomposition.⁷ Oettingen's results, however, do not confirm Landolt's statement that the decomposition is independent of the concentration of the acid. He criticizes the conception of a definitive "time of existence" or "life-period" of a chemical molecule, such as thiosulphuric acid, as the cause of the induction, and regards this as due to supersaturation of the solution with sulphur. This he supposes to pass through a metastable limit before spontaneous precipitation becomes possible. Contrary to Landolt, he found the induction decidedly dependent on the concentration of acid. For hydrochloric acid the curves relating the time of induction to the hydrogen ion concentration were found to be continuous curves, representable with fair accuracy by the equation

$$T = \frac{1}{A \log(1 + bC_H)}$$

Where A and b are constants and C_H is the hydrogen ion concentration obtained from conductance measurements. The independence of the nature of the acids is limited to the conditions that isohydric solutions be used, *i.e.*, concentrations equivalent with respect to hydrogen ion. The inhibiting action of sulphite is shown by a change in the constants A and b .

⁶ *Zeit. physik. Chem.*, **33**, 1, 1900.

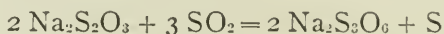
⁷ Within certain limits discussed later.

EQUILIBRIUM CONDITIONS.

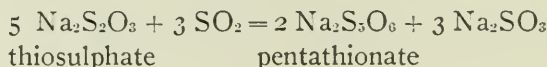
This action of sulphite is discussed by v. Oettingen from the point of view that the reaction



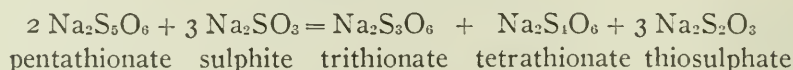
is reversible, so that the action of sulphite is due to mass action of the sulphite in increasing the reverse reaction. Qualitatively this agrees with the production of thiosulphate from sulphite and sulphur. Experiments by Colefax⁸ to determine the equilibrium showed that disturbing side reactions occur, *e.g.*,



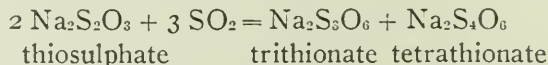
Foussereau⁹ followed the decomposition by conductivity measurements. The curves, with times as abscissæ and change of conductance as ordinate, show that with dilute mixtures of thiosulphate and acid the curves show decided inflection. This he attributed to supersaturation of sulphur, and autocatalysis by primary sulphur nuclei. He confirmed this by abbreviating the induction by the addition of partly decomposed solutions. That the reaction $\text{H}_2\text{S}_2\text{O}_3 = \text{H}_2\text{SO}_3 + \text{S}$, the decomposition of thiosulphate to sulphite and sulphur does not go quantitatively is easily shown; the iodine titration value should double for complete reaction, but actually it only increases some 80 to 85 per cent. It was shown early that small quantities of polythionates are formed¹⁰ and Raschig¹¹ considers that pentathionate is first formed, according to the equation



which then reacts with sulphite according to the reactions



so that the net result is given by



⁸ *Trans. Chem. Soc.*, **61**, 176, 199 (1892).

⁹ *Ann. Chim. Phys.*, **15**, 533 (1888).

¹⁰ G. Chancel and E. Deacon, *J. prakt. Chem.*, **90**, 55 (1863).

¹¹ *Zeit. angewandte Chemie*, **33**, 261 (1920).

An interesting case of chemical induction was discovered by Salzer¹² in connection with this. If a trace of potassium or sodium arsenite be added to thiosulphate before addition of acid, the decomposition into sulphurous acid and sulphur is largely inhibited, practically the whole of the thiosulphate becoming converted to polythionate. Soluble arsenates may also be used. This reaction has no actual value for the acid fixing bath, since although precipitation of sulphur is prevented, thiosulphate is actually rapidly removed. Hence it is rather the exclusion of arsenic, as an impurity, which is desirable. It appears then that in any case the influence of sulphite is due to its action as a product of a reversible reaction. Probably, however, colloid chemical considerations come into play in determining the rate of precipitation of sulphur, namely, the influence of the electrolytes present on the stability and coagulation of the sulphur hydrosol.

CONTROL OF HYDROGEN ION CONCENTRATION.

It is evident that, for a given quantity of protecting sulphite—a quantity which it is not desirable to exceed both from economic considerations, and from the fact that such excess will slow fixation by repressing swelling of the gelatin—there will be an upper limit to the permissible H-ion concentration, beyond which the protective action would exhaust too rapidly. This exhaustion or decline of the protective effect is due to more or less gradual volatilization of sulphurous acid, as well as oxidation of the sulphite. On the other hand, the concentration of H-ion must be *above* a certain lower limit, in order that the bath may be truly an acid fixing bath. The clearing action of acid on stains is primarily due to conversion of colored salts of dyes into colorless acids; while for definite known dyes the value of H-ion necessary can be specified,¹³ the products of developer oxidation are too indefinite for this. In the presence of sulphite as well there is possible also a specific bleaching action of sulphurous acid. A further necessity for a definite lower limit of H-ion is introduced by the alum. The hardening action of this is connected with hydrolysis in the gelatin, with retention of colloidal alumina. If the reaction is too alkaline the penetration of the alum is insufficient, and also the solution becomes unstable. Further, if as frequently happens, the

¹² *Chem. Ber.*, 19, 1696 (1886).

¹³ Cf. W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore.

alum is contaminated with iron, this *iron* will react with the polyphenolic bodies coming over from the developer, producing dark inky colorations. This effect is prevented by an acidity corresponding to $p_H \leq 6.0$. This is another instance of the influence of iron, as an impurity, upon the chemistry of photographic processes.¹⁴ The acidity must be sufficient to neutralize alkali from developer left in the film after rinsing with water. There is not only liability of the organic reducer to autoxidation, but by acting on the complex silver solution produced by the thiosulphite either actual intensification of the image may be produced, or colloidal silver deposited as dichroic fog.

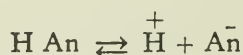
For physical chemical purposes it is most convenient to express the hydrogen ion concentration as a logarithmic function. The value p_H , introduced by Sørensen as the exponent of the hydrogen ion concentration,¹⁵ is given by

$$p_H = \log \left[\frac{1}{\left[\overset{+}{H} \right]} \right]$$

when $\left[\overset{+}{H} \right]$ is the concentration of hydrogen ion. The p_H value may be measured directly as the electrode potential of a hydrogen electrode immersed in a given solution¹⁶ or colorimetrically. We have determined the practically permissible limits of p_H in acid fixing baths, both in the absence and in the presence of alums and hardeners. It is necessary to consider here the interaction of the bath with gelatin, but before doing this we must notice the question of *reserve* acidity.

RESERVE ACIDITY OF FIXING BATHS.

The undissociated part of an acid furnishing H-ion according to the equilibrium



where An^- is an anion, is the "reserve acidity" which is called into action as fast as the equilibrium is disturbed by removal of the dissociation products. The neutralization of entrained alkaline developer in film, plate or paper will evidently remove H-ion.

¹⁴ Cf. S. E. Sheppard, "Effect of Iron Content of Ammonium Persulphate," *Brit. J. Phot.*, 65, 314 (1918).

¹⁵ Cf. W. M. Clark, *op cit.*

¹⁶ According to Nernst's equation.

Hence, in order that the concentration of this (or the p_H value) may not change seriously before the actual fixing efficiency of the bath is exhausted, the acid component should have the requisite reserve acidity. Otherwise expressed, we must be able to take sufficient total acid, but suitably regulate actual acidity or H-ion concentration, to prescribed limits.

Organic acids, as weak acids, are the most suitable for this purpose, and are easily regulated, or "buffered" by addition of a suitable amount of their sodium salts. Data of Walpole¹⁷ illustrated how the $\left[\text{H}^+ \right]$ varies in a solution of acetic acid and sodium acetate. Taking 10 c.c. of N/5 acetic acid, and adding various amounts of caustic soda, we have:

TABLE IV.

N/5 NaOH	Ratio $\frac{\text{Salt}}{\text{Acid}}$	p_H
c.c.		
0.20	0.020	3.08
0.50	0.053	3.42
1.0	0.111	3.72
2.0	0.250	4.05
3.0	0.429	4.27
4.0	0.667	4.45
5.0	1.000	4.63
6.0	1.500	4.80
7.0	2.33	4.99
8.0	4.00	5.23
9.0	9.00	5.57

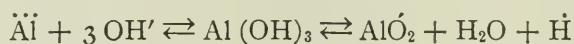
HARDENING ACTION OF ALUM ON GELATIN.

Hardening agents for gelatin may be divided into temporary and permanent hardeners. A temporary hardener acts simply by repressing swelling; concentrated solutions of many neutral salts, *e.g.*, of sodium sulphate, alone or in presence of acid, operate in this way. Since a concentrated jelly melts at a higher temperature than a more dilute one,¹⁸ hardening is secured for the duration of these conditions, but is readily reversed by soaking in water. Permanent hardening, which is of a similar character to the tanning of leather, is not simply reversed, and involves fixation of other substances by the gelatin. The question as to whether the fixation

¹⁷ Cf. W. M. Clark, "Determination of Hydrogen Ions," p. 17.

¹⁸ Cf. S. E. Sheppard and S. S. Sweet, *J. Ind. Eng. Chem.*, 13, 423 (1921).

of aluminium, chromium and iron compounds by gelatin is due to chemical combination, or to adsorption,¹⁹ has been much debated. Without endeavoring to settle this forthwith, we must notice that recent work²⁰ has shown that the reactivity of the amphoteric gelatin is markedly dependent upon the hydrogen ion concentration of the solution with which it is in equilibrium. Broadly stated, it appears that for $p_H > 4.7 - 4.8$ the isoelectric point, gelatin is a cation, and combines with anions, for $p_H < 4.7 - 4.8$, gelatin forms anions, combining with cations.²¹ At the neutral, or isoelectric point, it is in its least reactive condition. From this, we should expect that gelatin would combine with $\ddot{\text{Al}}$ -cation for $p_H > 4.8$ and in fact Loeb²² has given some data on the effect of AlCl_3 on gelatin solution supporting this view. The evidence, however, appears to us inadequate, because Loeb used solutions of steadily *decreasing* concentration of AlCl_3 , and simultaneously *increasing* H-ion. Deductions from experiments with such a complication seems questionable. Our own experiments on the hardening of gelatin by aluminium, etc., solutions, show the matter to be more complicated. The state of the aluminium in solution has itself to be taken into consideration, since aluminium hydroxide is itself an amphoteric substance. Most simply formulated, we have²³



from which it would follow that there is a certain hydrogen ion concentration at which hydrous alumina has the least tendency to form either $\ddot{\text{Al}}$ ions or AlO'_2 anions, *i.e.*, the isoelectric point. As to the p_H value of this point, the evidence is incomplete and inconclusive. J. H. Hildebrand²⁴ showed that alumina is precipitated by sodium hydroxide from aluminium sulphate solution when the hydrogen ion concentration varied roughly during precipitation between 10^{-3} and 10^{-5} , *i.e.*, $p_H = 3$ to 5.

¹⁹ See discussion by H. R. Procter, "First Report on Colloid Chemistry in its Industrial Applications," *Brit. A. A. Science*, 1917, p. 12.

²⁰ Cf. J. Loeb, "Proteins and the Theory of Colloid Behavior," New York, McGraw Hill Co., 1922.

²¹ Where dyes and amphoteric compounds are in question, this statement requires qualification.

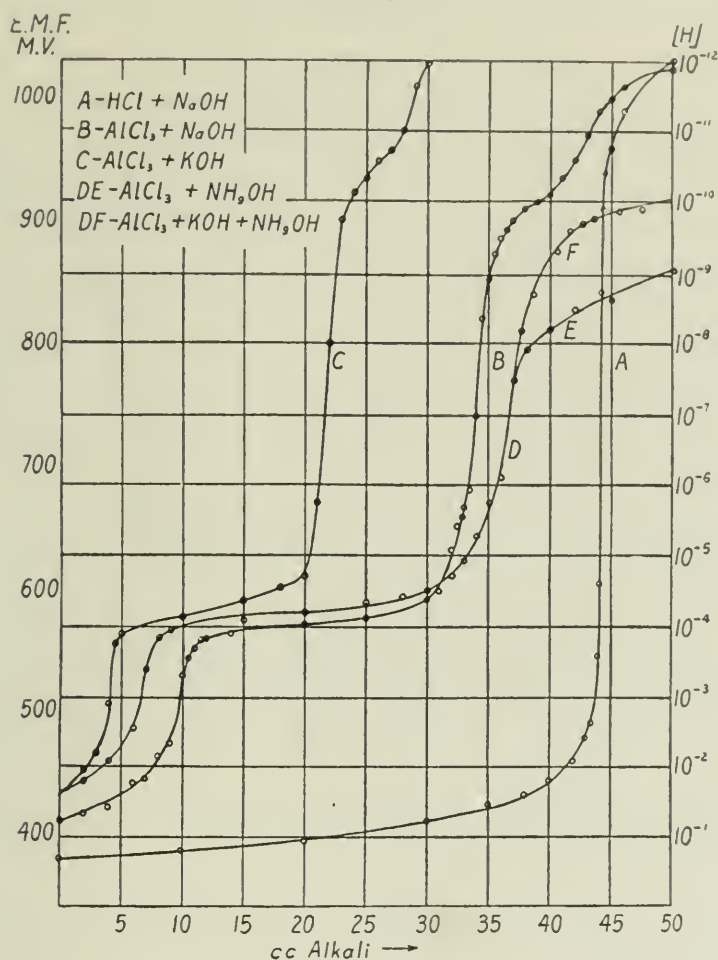
²² *J. Gen. Physiolog.*, I, 503 (1919).

²³ J. Stieglitz, "Elements of Qualitative Analysis," p. 171 (1911).

²⁴ *J. Am. Chem. Soc.*, 35, 24 (1913).

The work of Blum²⁵ on the reactions of aluminium compounds with certain bases led to somewhat greater precision. His data on the changes in hydrogen ion concentration occurring on addition of alkalis to AlCl_3 solutions are reproduced graphi-

FIG. 3.



(From Blum.)

cally in Fig. 3. From these it appears that the course is largely independent of the alkali used; in general, precipitation²⁶ begins when $p_H = 3$, and is complete before $p_H = 7$.

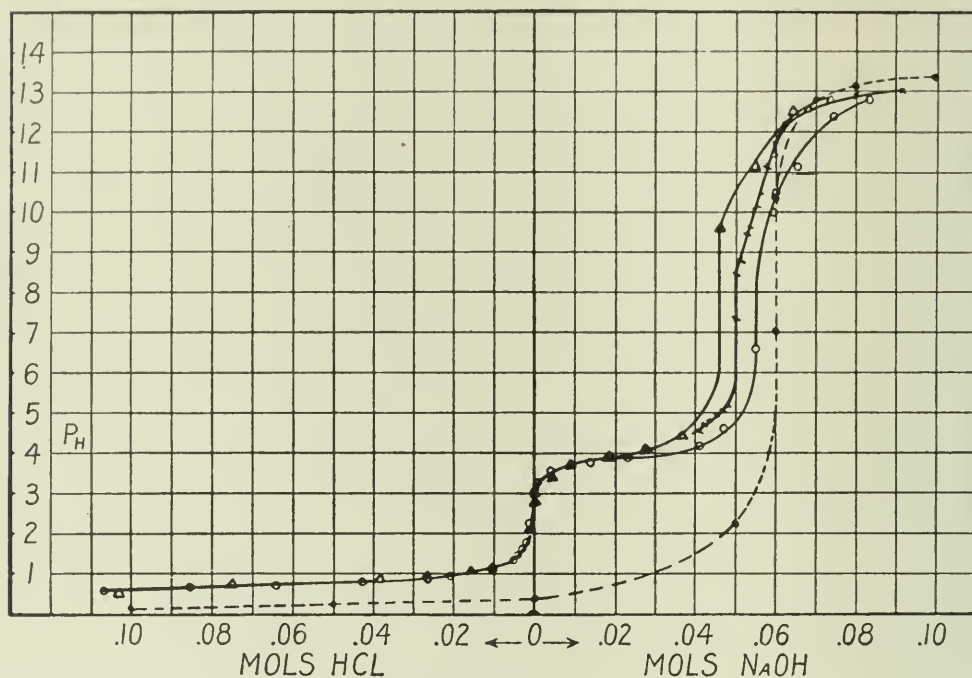
Now we have made up hardening solutions from alum ($\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$) in which, first, the acidity (H-ion) was varied

²⁵ *J. Am. Chem. Soc.*, **35** (1913); *Sci. Pap. Bur. Stand.*, No. 286 (1916); *J. Amer. Chem. Soc.*, **38** (1916).

²⁶ By this Blum states that chemical formation of $\text{Al}(\text{OH})_3$ is meant, not necessarily visible coagulation, which is variable, and may not occur until one-third to one-half the alkali for complete precipitation has been added.

by addition of acid (HCl) and alkali (NaOH), respectively; p_H measurements were made electrometrically, and the curves plotted (Fig. 4). Some differences from Blum's curves for $AlCl_3$ and bases exist, but not large, and partly accountable if the samples of $AlCl_3$ and Al_2SO_4 used had slightly different free acid contents. But also there is probably an influence of the anion. This

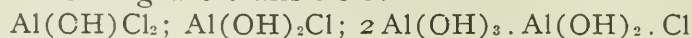
FIG. 4.



- $AlCl_3 \cdot xH_2O$.57 gr. in 105 gr. H_2O practically M/10 Al.
 △ $Al-(SO_4)_3 \cdot xH_2O$.57 gr. in 105.98 gr. H_2O practically M/10 Al.
 × $Al_2(SO_4)_3 \cdot xH_2O$.57 gr. in 105.98 gr. H_2O practically M/10 Al (this solution stirred).
 ● .6M HCl, the equivalent of the Al salt.

conclusion is strengthened when the electrometric titration is carried out in presence of substances like *citric acid* having strong complex-forming tendency with alumina.

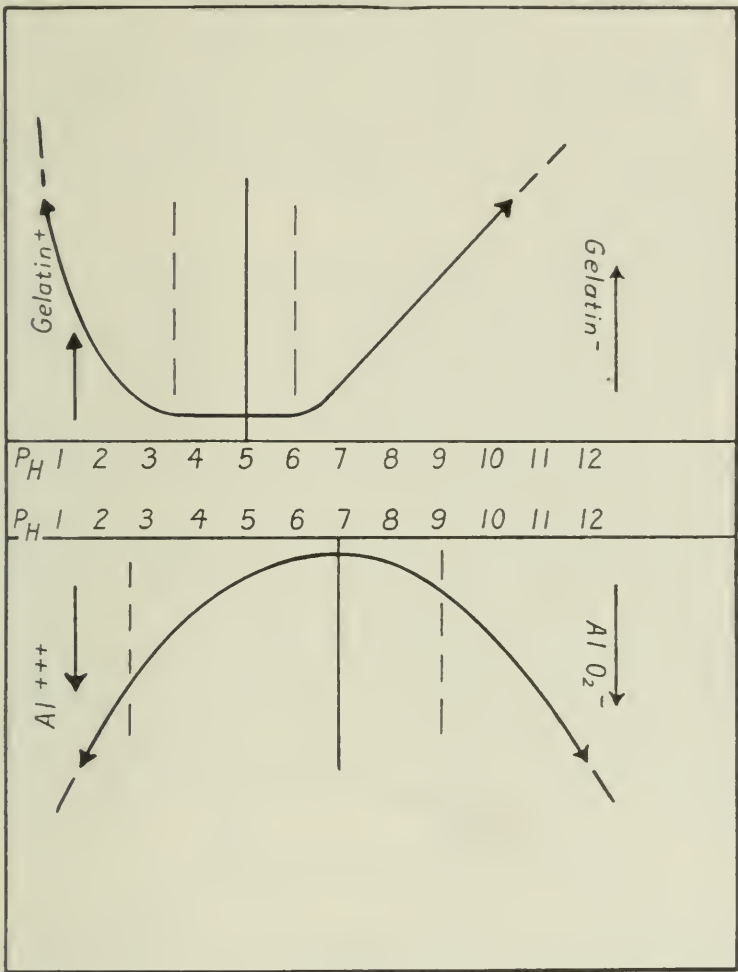
It is probable that the neutral complex is not simple $Al(OH)_3$, in these cases, but so-called basic salts. Even in the case of $AlCl_3$ and NaOH Wo. Pauli²⁷ has found evidence that the sols of "colloid" alumina, prepared by hydrolysis of aluminium salts, may be regarded as aggregates of intermediate complex ions, following the transition:



²⁷ Cf. "Physics and Chemistry of Colloids" (report of general discussion at Faraday Society), published by Department of Scientific and Industrial Research, Gt. Britain, 1921, p. 16.

“ In all cases the metal hydroxides show a tendency to transform themselves, by the addition of an inorganic molecule, into charged particles, an aggregation of which forms the colloid complex ” . . . “ with increasing concentration of $\text{Al}(\text{OH})_3$, the aluminium oxy-salts incline to the formation of *negative* aluminate complexes, in addition to the positive ones. This tendency in-

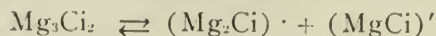
FIG. 5.



creases with increasing dilution, so that certain aluminium hydroxide sols stand at the boundary between positive and negative colloids.” In this connection the discussion by C. Blomberg²⁸ of cases of complex ionization with two complex ions is of interest. Magnesium citrate, calcium citrate, show few if any ions of the metal. Similarly aluminium precipitation as $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

²⁸ Zeit. f. Elektrochem., 21, 437 (1915).

is prevented by citrates, as also its alizarine lake formation. We have, therefore, as probable primary ionization



and secondarily only, dissociation of free Mg and citrate ions. Similarly with Al :



are possible complexes, the formation of which will be helped by excess citrate ion.²⁹ With varying H-ion, inversely, OH-ion, neutral molecules $[\text{Al}_2 \text{ Ci H}]$ to $\text{Al Ci}_2(\text{OH})$ can be formed, and this may explain the effect of the citrate addition in displacing the p_H curve. The apparent opposite effect of sulphite and thiosulphate (curves determined colorimetrically) is less comprehensible.³⁰

We may summarize these results roughly by Fig. 5. In the upper half the line at $p_H = 4.8$ gives the isoelectric value dividing electropositive gelatin from electronegatively charged gelatin. Below is the diagram for alumina. Aluminium cations exist up to $p_H = 3$, in absence of citric, etc., acid; no definite isoelectric point can be assigned on other grounds, but $p_H = 6$ to 8 seems the most probable from ionization data. Loeb states $p_H = 7$ (the point of complete precipitation, according to Blum) is the isoelectric point, but gives no definite reasons. It is apparent, from the diagram, when both gelatin and aluminium salts are present together, as well as other ionogenic and complex-forming components, that a complicated and slowly adjusted series of equilibria is likely. The formation of "aluminium gelatinates," as suggested by Loeb,³¹ appears likely to be limited to a narrow p_H range.

EXPERIMENTAL HARDENING.

This conclusion is borne out by experiments on alum hardening, in which the H-ion of the solutions was measured and plotted as abscissa against *melting point* as ordinate. From Fig. 6 it will be seen that in absence of alum, the maximum *m.p.*—at 34°C .—

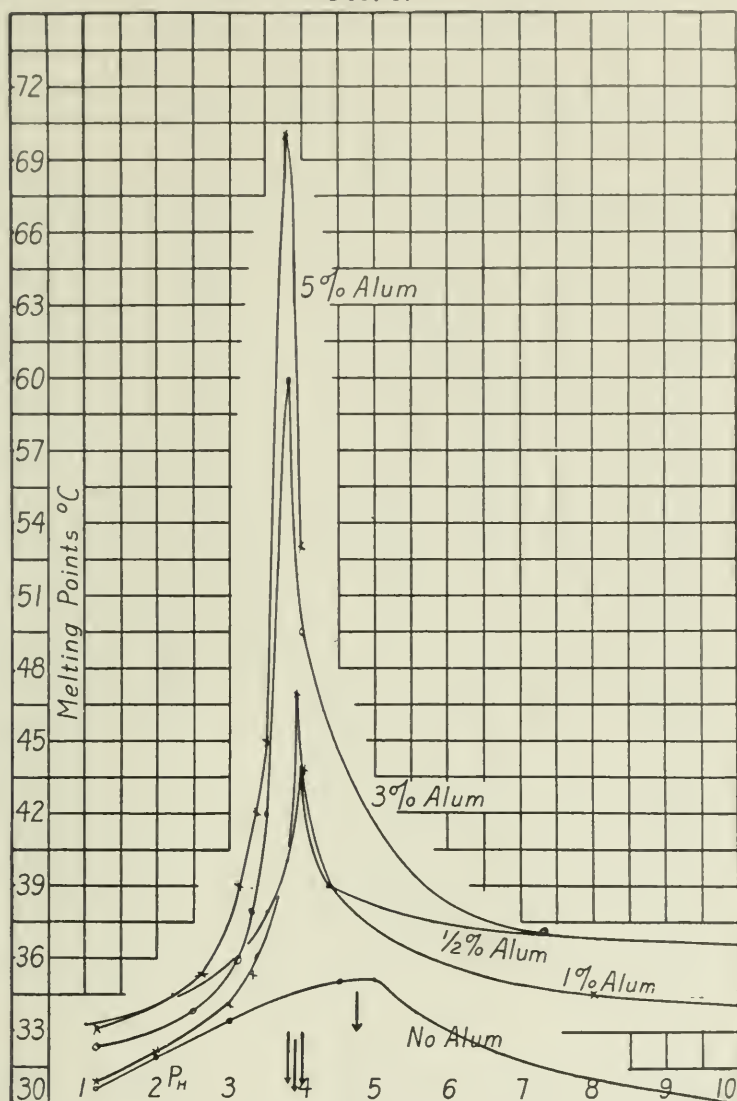
²⁹ These equations are suggestive only. Much work on solubilities, transport numbers, conductances, etc., is required to establish the actual conditions.

³⁰ The formation of aluminium thiosulphate and basic sulphites may play a part here.

³¹ Loeb's diagram (*loc. cit.*) appears to be somewhat misleading, postulating a "region" of aluminium-gelatinates extending indefinitely from $p_H = 5$ to increasing values of p_H .

was at the isoelectric point of gelatin $p_H = 4.8$. With alum, and using HCl and NaOH to adjust the p_H , results expressed in Fig. 6 were obtained. The tendency is for the maximum hardening to occur near $p_H = 4.0$, but the value diminishes as the alum

FIG. 6.

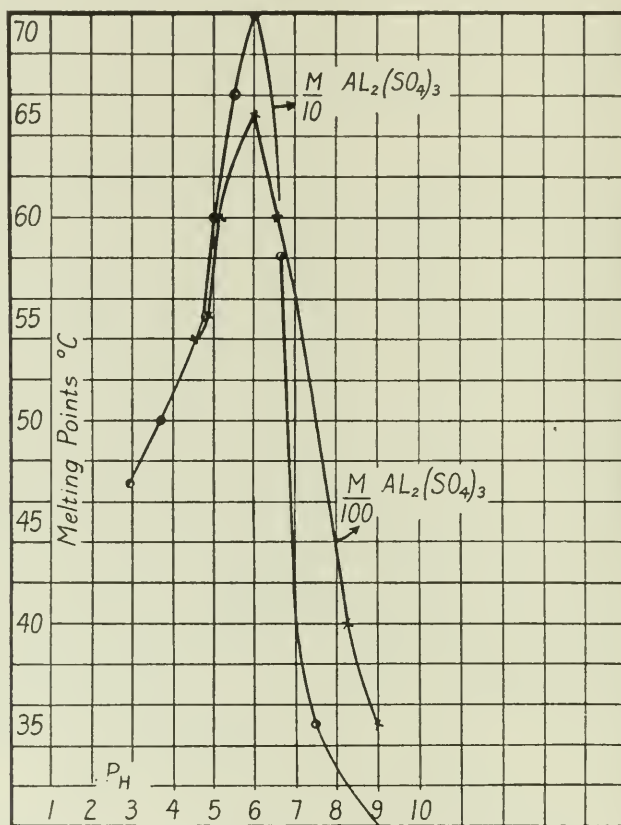


concentration is increased. From this it seems probable that the hardening is effected by Al^{+++} , $Al(OH)^{++}$, $Al(OH)_2^+$ ions interacting with negative gelatin ions (including such complexes as $3 Al(OH)_2 Al(OH)_3$). This necessitates the existence of gelatin anions at $p_H < 4.8$, but this is possible in the neighborhood of the isoelectric point.³²

³² The possibility that a complex aluminous anion is reacting with electro-positive gelatin may also be considered, but is little likely.

On the other hand, if an alum salt, *e.g.*, $\text{Al}_2(\text{SO}_4)_3$, is added, with stirring, to a solution of gelatin, to which definite amounts of acid or alkali have been added previously, the dependence of the *melting point* of the jellies upon the p_H (of the jelly solution) is considerably different. As shown in Fig. 7 the maximum now occurs at $p_H=6$, consequently we may regard the value $p_H=4$ found before, for solutions, as due to removal of diffusible Al-ions by precipitation. The results shown in Fig. 7 are in

FIG. 7.



agreement with the diagram in Fig. 5. But positive Al-ions may be removed not only by precipitation, but by soluble complex formation, *e.g.*, with organic acids.

ORGANIC ACIDS.

As we have seen, if hypo (thiosulphate) is to be present, it is desirable to use organic acids, so that the p_H may not fall below a limit leading to sulphur precipitation. For solutions *acetic acid* is preferable, but for fixing salt powders citric acid has been much used. Taking 3 per cent. alum, the effect of different per-

centages of citric radical, or citrate ion, over a wide p_H range, is shown in Fig. 8.

It will be seen that the hardening action of aluminium salts is very rapidly decreased by increasing citric ion. In the presence of sulphite and thiosulphate, the p_H for maximum hardening is raised, and the region of hardening extended somewhat (Fig. 9).

FIG. 8.

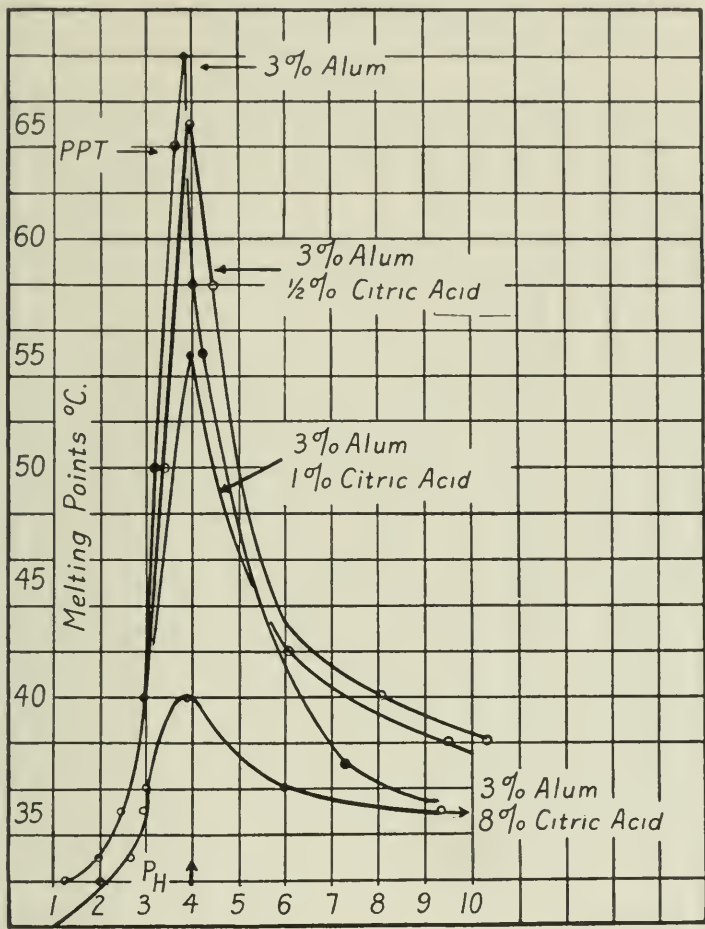


TABLE V.

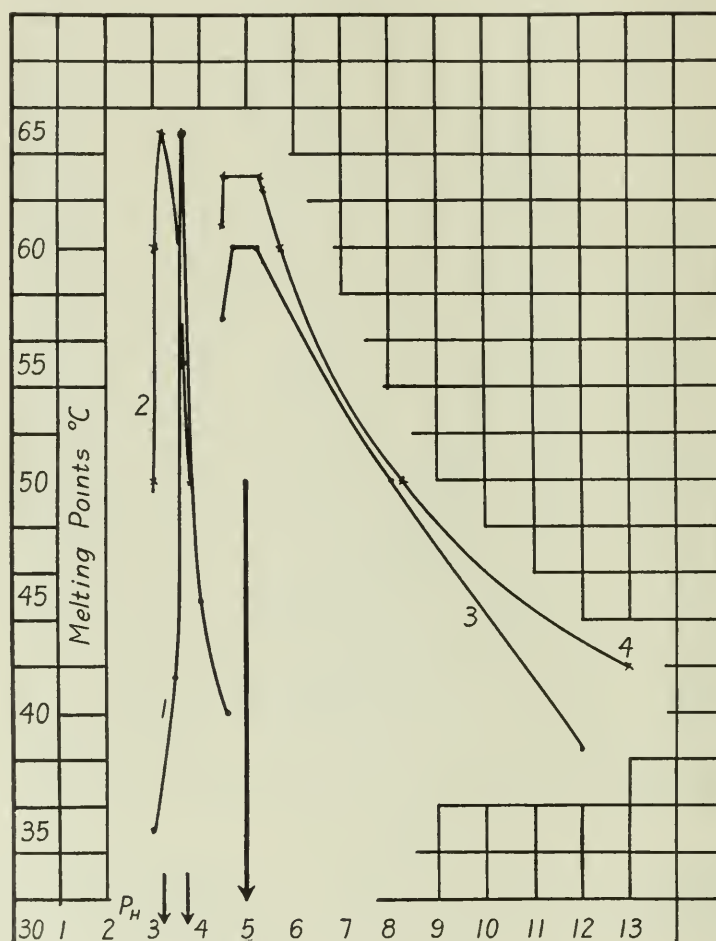
Component.	Grams per 1000 c.c.							
	0	240	240	240	240	240	240	240
Hypo	0	240	240	240	240	240	240	240
Alum	0	8	8	8	8	8	8	8
Sodium bisulphite	50	50	30	30	30	30	30	30
Sodium citrate	0	5	2	5	10	20	20	20
Time of fixation in mins.	5	8	5	5	4.5	6	6	6
Melting point of emulsion ° C. .	42°	37°	55°	40°	38°	35°	35°	35°
Precipitation	+	—	—	—	—	—	—	—

This table shows the effect of citrate ion in reducing the hardening action of aluminium on a gelatin emulsion, the melting point of which in water was about 34° C.

Investigation showed that while *formate* and *acetate* did not interfere very much, all of the following acid radicals had a similar inhibiting effect:

Oxalic	$(\text{COOH})_2$
Lactic	$\text{CH}_3.\text{CH}.\text{OH}.\text{COOH}$
Citric	$(\text{CH}_2.\text{COOH})_2.\text{C}(\text{OH})\text{COOH}$
Tartaric	$\text{COOH}.\text{C}(\text{OH})_2.\text{COOH}$
Malic	$\text{COOH}.\text{CH}_2.\text{CHOH}.\text{COOH}$
Maleic	$\text{COOH}.\text{CH}:\text{CH}.\text{COOH}$

FIG. 9.



1. 3 per cent. alum, 0.5 per cent. citric acid, 1 per cent. Na_2SO_3
2. 3 per cent. alum, 0.5 per cent. citric acid, 2 per cent. Na_2SO_3
3. 3 per cent. alum, 0.5 per cent. citric acid, 1 per cent. Na_2SO_3 , 25 per cent. $\text{Na}_2\text{S}_2\text{O}_3$
4. 3 per cent. alum, 0.5 per cent. citric acid, 2 per cent. Na_2SO_3 , 25 per cent. $\text{Na}_2\text{S}_2\text{O}_3$

This action is to be attributed to the formation of complexes, as already noted. Now practically, it is necessary that the acid fixing bath have a considerable amount of organic acid, in order that the reserve acidity may take up alkali from the developer.

Again, each hardening operation removes a certain amount of alumina. Hence, for maximum hardening the acid fixing bath should have a considerable quantity of organic acid,³³ and as large an amount of aluminium or chromium salt as is consistent with maintaining a $p_H = 4$ or slightly greater. Acid making the $p_H = 3$ is unsafe, while acidity $p_H > 5$, while it may not precipitate alumina,³⁴ will give poor hardening.

The following assemblage of desiderata or specifications for an acid fixing and hardening solution shows that while the theoretical investigation can indicate the governing conditions, practically a compromise has to be effected.

1. Long fixing life,³⁵ that is, as high a concentration of "hypo" as possible.

³³ Or, as noted later, of sulphurous acid (bisulphite) plus salt of organic acid.

³⁴ Or basic aluminium salts.

³⁵ The limits of useful life of a fixing bath in respect to silver saturation have been investigated by Gaedicke (*Eder's Jahr.*, 1906, p. 4) and by Messrs. Lumière and Seyewetz (*Photo. J.*, 47, 129 (1907)). The former deduced the limits from the discoloration of a test impregnated with thiosulphate, dipped in various strengths of silver nitrate, and exposed to light and air. The latter worked directly with silver bromide. They found a larger amount of silver, as bromide, could be added to thiosulphate, without decomposition, than as nitrate. Thus Gaedicke found that to a solution of 15 per cent. hypo, only 1/10 of the silver nitrate causing complete saturation can be added without permitting discoloration of the paper tint. Lumière and Seyewetz found that 60 per cent. of the silver bromide saturation can be added without producing discoloration, for 15 per cent. solution, but only 24 per cent. of that saturating a 45 per cent. hypo solution. Addition, to the 15 per cent. hypo solution, of 1.5 per cent. bisulphite lowered the limit to 27 per cent. (of saturation), while further addition of .5 per cent. chrome alum raised it again to 38 per cent. These latter results seem somewhat peculiar.

Practically, they deduce that the number of 9×12 cm. plates which can be fixed without fear of stain by

(a) 1 litre of 15 per cent. hypo = 100

(b) 1 litre of 15 per cent. hypo = 60

1.5 per cent. bisulphite

(c) 1 litre of 15 per cent. hypo

1.5 per cent. bisulphite = 75

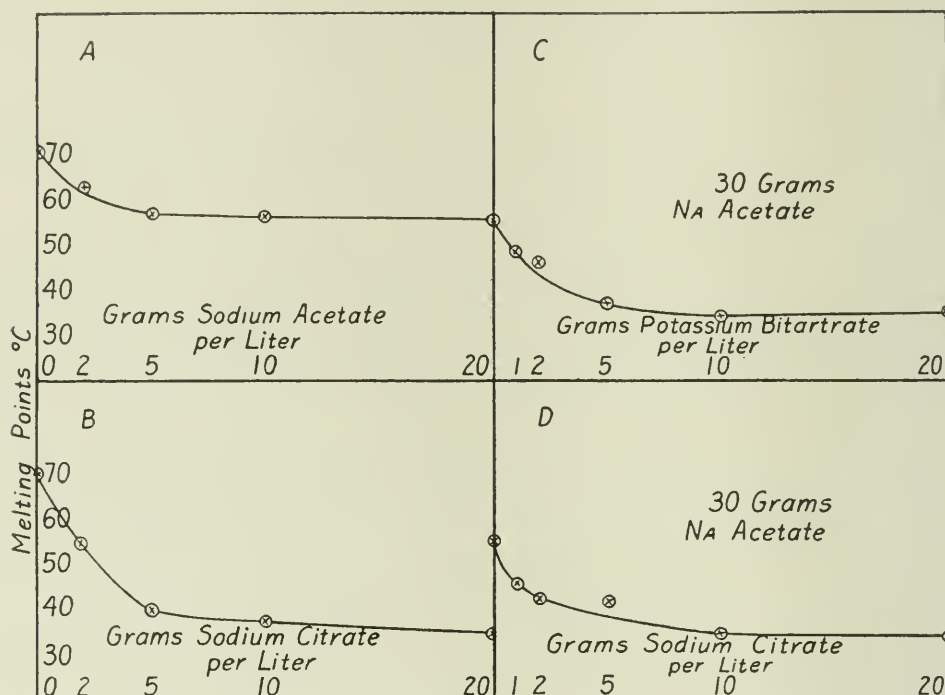
0.5 per cent. chrome alum

Using 25 per cent. hypo this would correspond to about 15,000 sq. cms. plate or film per litre. The limit will be somewhat lower for X-ray plates, at 40 + per cent. silver halides, and higher for certain others. But approximately this works out to about 9000 sq. ins. per gallon of 25 per cent. hypo, with bisulphite, and this figure has been confirmed in this laboratory.

2. Rapid fixation hence, other things equal, "hypo" concentration should not be much above 30 per cent. Practically, the time to clear the residual silver halide should not be much more than five minutes; with a safety allowance, therefore, total time equals about ten minutes. But with strongly hardening solutions some increase in time over this is probable.

3. The bath must not deposit alumina or basic aluminium compounds, even after considerable developer alkali has been

FIG. 10.



added. This means as much organic acid radical as is otherwise compatible.

4. Since the organic acid radical must be high, small amounts of alumina will have no effective hardening action. Hence, the quantity of aluminium salt should be large.

5. The hydrogen-ion concentration should correspond approximately to a $p_H = 4$. In the presence of sulphite and thiosulphate, as will be noted, there is an apparent displacement of the p_H of maximum hardening to slightly greater p_H values. If the bath is started to have a $p_H = \text{ca } 3.5$, it will change in the right direction as acid is neutralized and more of the "buffer" salt formed.

A bath of given "hypo" concentration, 25 or 30 per cent.

being high enough, in view of the anti-swelling action of the additional components, will fix a definite number of plates or films of given size, before becoming too saturated with silver. This limit will be reduced with increasing acidity, beyond a certain point, because of staining due to silver sulphide formation. Again, this number of plates or films will carry over a certain amount of alkaline developer and the acid reserve must be adjusted to take care of this. Further, this number will remove a certain amount of alumina, and the alum content must be adjusted to take care of this. Actually, all the conditions cannot be completely satisfied, and something has to be sacrificed, generally on the "hardening" side.

As illustrating the influence of different organic acid radicals on the hardening, the curves in Fig. 10 are given: Bitartrate; citrate; acetate.

In the bath used, 25 per cent. "hypo" is balanced with 8 per cent. potash alum, 30 per cent. NaHSO_3 , giving sufficient acidity ($p_H = 3.1$, but buffered with sodium acetate to $p_H = 3.5$ to 3.7).

Incidentally, it may be noted that the "hardening" bath is chiefly necessary for plates and films. With the exception of some grades of bromide paper, which show an *M.P.* of about 40° to 45° C., practically all developing-out papers are hardened to withstand temperatures of 95° C. +, above boiling point for a short time. For plates and films, requiring considerable alum hardening, therefore, a high concentration of aluminium salt is necessary with sufficient complex-forming organic acid to hold up precipitation, and to maintain a hydrogen ion concentration of $p_H = 3.5$ to $p_H = 4.5$. Practically, not more than 5 per cent. of alum is desirable, and as shown, this limits the amount of citrate ion to less than 1 per cent. of the total solution.

For a long time the band spectrum of nitrogen has been known, but our acquaintance has been incomplete, as is shown by the discovery of three additional bands at 5075, 5018 and 4961 Ångstrom units in the Palmer Physical Laboratory, Princeton, by O. S. Duffendack (*Phys. Rev.*, Dec., 1922).

G. F. S.

In an experimental study of the scattering of homogeneous X-rays, C. W. Hewlett came upon the interesting fact that three liquids, benzene, mesitylene and octane, comport themselves in such a manner as to resemble crystals in their action upon X-rays.

G. F. S.

The Validity of Ohm's Law for Intense Electric Fields in Electrolytes. MAX WIEN. (*Physikal. Zeit.*, Oct. 15, 1922.)—The author sets himself the problem of using a field of about 100,000 volts per cm. This high value necessitates the use of a condenser discharge so that in the brief time during which the current flows, thermal and electrolytic effects may not intervene. The general plan of the investigation is the following: Let two resistances that are equal when measured by a Kohlrausch Bridge be prepared, of which one is the electrolytic resistance to be investigated and the other a comparison resistance. One of these is inserted in the circuit traversed by the discharge of the condenser and the current strength is measured. Then the other resistance replaces the first and the discharge is repeated. If the current strength is the same in the two cases the ratio of resistances of the two inserted resistances is the same at the higher field strength as at the lower when they were found to be equal, and since the comparison resistance has not changed, it is concluded that the electrolytic one also has remained unchanged. The conclusion is, "I believe that I have presented proof that Ohm's law holds within one per cent. for electrolytes up to field strengths of about 500,000 volts per cm." G. F. S.

A New Method of Determining $\frac{e}{m}$. H. BUSCH. (*Physikal. Zeit.*, Oct. 15, 1922.)—In a Braun tube a diverging beam of cathode rays falls on a fluorescing screen. Let a magnetizing coil with its axis parallel to the axis of the rays surround them. Its effect will be to twist each ray into a spiral with its axis parallel to the direction of the magnetic lines of force. All rays coming through the same point of the diaphragm will complete one turn around the spiral in the same time so that a fluorescent screen placed just where it receives the rays at that instant will show a sharp image of the diaphragm. This is true on the assumption that the rays actually diverge from the diaphragm of the tube. As a matter of fact, the point of divergence is only near to it. This is remedied by applying a rotating magnetic field to the beam before it reaches the diaphragm. This done, a sharp image of the latter can be got on the screen by varying the strength of the longitudinal magnetic field through regulation of the current in the coil. The ratio of the elementary quantity of electricity to the mass of an electron $\frac{e}{m}$ then can be calculated from three measurable quantities, current strength, distance from diaphragm to screen and the potential of the discharge. The canonical value of the ratio is 1767×10^7 electromagnetic units per gram. A series of determinations gives for the mean value 1768 instead of 1767. The method was demonstrated at the session of German physicists in Leipzig last September. It was presented as suitable for demonstration purposes and for students' use, but in addition, it seems promising as a method of exact measurement. G. F. S.

A RELATION BETWEEN THE BRIGHTNESS AND HIDING-POWER OF WHITE PAINT-PIGMENTS.*

BY

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It is generally recognized¹ at the present time that a mere statement of the hiding-power of a white paint-pigment will not suffice to establish the excellence of the product. Any colored contamination such as dust, stain, metallic particles, etc., will increase the hiding-power at the expense of brightness. Hence, it is necessary to state the numerical values both for brightness and for hiding-power. For purposes of comparison of the hiding-powers of two different paints it is customary² to add sufficient mineral or bone-black to the brighter sample so as to reduce its brightness to that of the duller and then to make measurements of hiding-power. This procedure is very laborious. In view of the importance of the subject it seemed altogether worth while to seek for a possible simple relationship between the above-mentioned properties.

The procedure followed consisted simply in measuring hiding-power and brightness of a given paint. The paints were initially prepared by Mr. H. A. Gardner and consisted merely of the pigment ground in pale linseed oil—the mixture being subsequently reduced to “brushing consistency” by the addition of more oil. The relative proportions of pigment and oil are given in Table I. To these samples, very small quantities of bone-black were added and similar measurements were carried out. The cryptometer³ was used for hiding-power measurements while the writer's colorimeter⁴ was used to carry out brightness (*i.e.*, coefficient of diffuse reflection) measurements. Because of the

* Communicated by Dr. Joseph S. Ames, Associate Editor of this JOURNAL.

¹ H. A. Gardner, “Physical and Chemical Examination of Paints, etc.,” 1922.

² J. H. Calbeck, *Proc. Am. Soc. Testing Materials*, 1922.

³ A. H. Pfund, JOURNAL FRANKLIN INST., Nov., 1919, p. 675.

⁴ A. H. Pfund, JOURNAL FRANKLIN INST., Mar., 1920, p. 371; *Proc. Am. Soc. Testing Materials*, 1920.

fluidity of the paint mixtures, the upper colorimeter plate was coated with fumed MgO, while the paint was poured into the lower plate or saucer. The brightness measurements are probably accurate to ± 1 per cent. while the hiding-power measurements may be uncertain by as much as ± 5 per cent.

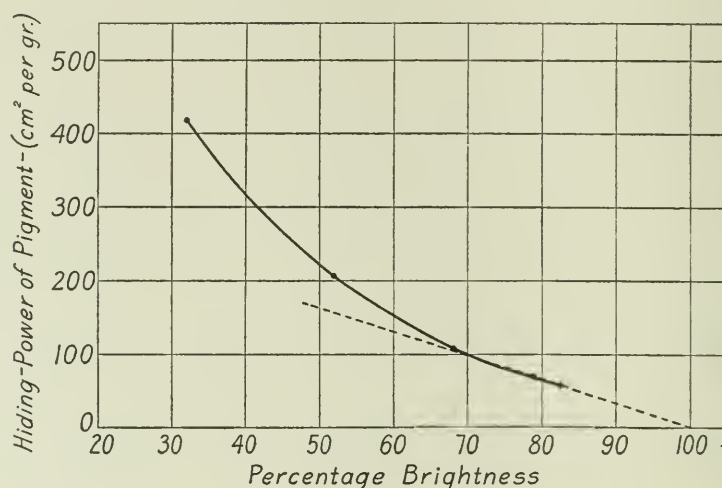
TABLE I.

Number.*	Pigment.	Percentage by Weight.	
		Pigment.	Oil.
1	Basic sulphate white lead	69.7	30.3
2	Basic carbonate white lead.....	70.4	29.6
3	Electrolytic white lead.....	71.3	28.7
4	Timonox.....	64.5	35.5
5	Zinc oxide (French process)	50.2	49.8
6	Modern process lithopone	61.6	38.4
7	Titanox	60.1	39.9

* These numbers correspond to the curves in Figs. 2 and 3.

A typical curve, covering a considerable range, both in brightness and in hiding-power, is shown in Fig. 1. This paint con-

FIG. 1.



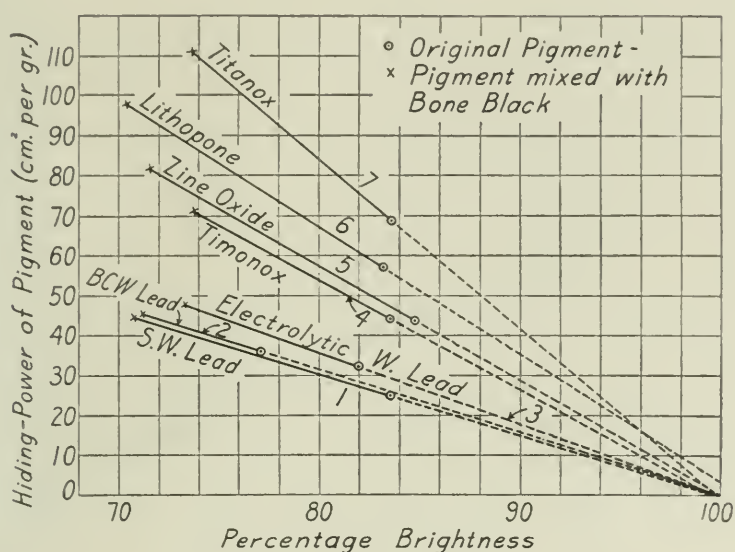
sisted of zinc oxide in linseed oil and is not included in the above list.

It is at once evident from this curve that, if we limit our considerations to that portion of the curve which lies between the brightness 70 per cent., *i.e.*, point *A*, and the terminal point *B*, the (dotted) straight line defined by these points passes through the point: zero hiding-power, 100 per cent. brightness. In order

to ascertain whether or not this relationship held for other paints also, similar tests were carried out on Gardner's paints. But two determinations were made for each paint: One, with the uncontaminated paint and the other with the grayed paint—care being taken to keep the brightness greater than 70 per cent. The results are presented in Fig. 2 and indicate clearly that, within the limits of accuracy, the relation holds quite generally.

There are several points of interest here to which attention might be called. In the first place, it is to be observed that while

FIG. 2.



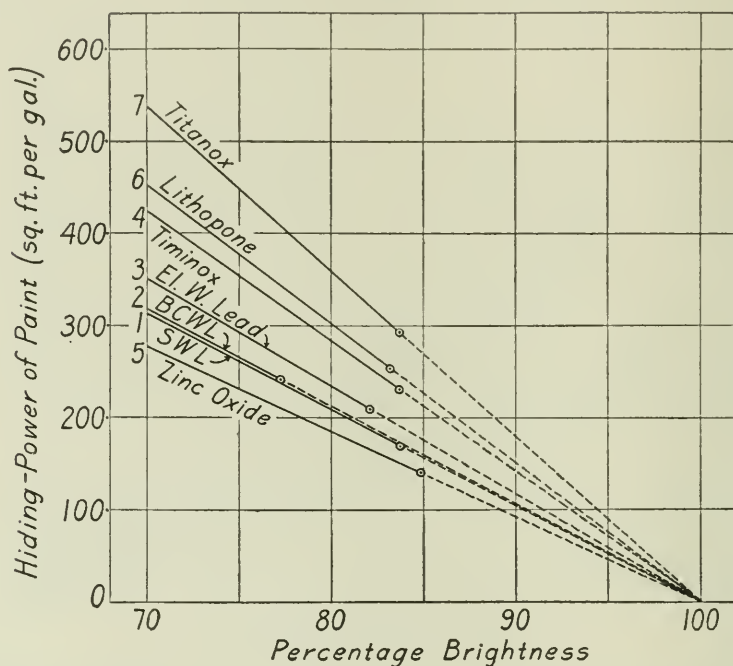
basic sulphate white lead (S.W. Lead, 1) is initially inferior in hiding-power to basic carbonate white lead (B.C.W. Lead, 2), it, *i.e.*, S.W. Lead, attains essentially the same hiding-power when its brightness is reduced to that of B.C.W. Lead.⁵ Again, in the case of B.C.W. Lead (2) and Electrolytic White Lead (3) we note that, while both have the same chemical constitution, the latter is "cleaner" and has a smaller particle size. While sample (3) initially has the smaller hiding-power, it attains a higher value when the brightness is reduced to that of sample (2).

If the preceding data be recalculated so as to yield the hiding-power of the paint rather than that of the pigment, curves of the type shown in Fig. 3 are obtained. Contrasting these curves with the previous set, it is evident that the order has been changed

⁵ This verifies the results of a direct comparison of these two pigments by J. H. Calbeck, *Proc. Am. Soc. Testing Materials*, 1922.

in consequence of the differences in the pigment-vehicle ratios. The point to be emphasized in this connection is that, while these curves are only approximations, they hold within the limits of accuracy of cryptometer settings. Since these curves are all essentially straight lines passing through the 0-100 point, it is sufficient to make but a *single brightness-hiding-power determination* at any degree of contamination (brightness greater than 70

FIG. 3.



per cent.) in order to establish the curve. This was done in plotting the curves in Fig. 3.

Such curves as these are of value, not only in making possible a comparison of hiding-powers at the same brightness, but in predicting the effect of removal or addition of contamination *so long as all other characteristics of the pigment remain unaltered*. To be specific, electrolytic white lead is essentially "clean," therefore the *extrapolated portion of the curve is meaningless*. The only manner by which the brightness of such a pigment might be increased would be to decrease the particle size. Such a change, however, would immediately result in an increase in hiding-power. This new pigment would then give rise to a new curve whose slope is steeper than that of its predecessor. (It is, of course, well known that the diminution in particle size is of advantage

only up to that point at which the particle size is of the order of the wave-length of light. A further diminution results in a decrease both in brightness and in hiding-power.)

While the extrapolated portions of the preceding curves pass through the 0 – 100 point, it is probably not true that, if a paint of 100 per cent. brightness could be realized, the hiding-power would be zero. The general form of the full curve shown in Fig. 1 would seem to indicate that the hiding-power is greater than zero at 100 per cent. brightness. This statement, however, does not affect the conclusions previously reached. It has already been pointed out that the extrapolation is meaningless beyond the point at which the pigment is “clean.” The fact that the simple straight-line relation holds only for brightness values greater than 70 per cent. is no serious handicap since all modern paints, marketed as “white,” have a brightness greater than 70 per cent. Any paint falling below this limit falls very definitely into the class of grays.

The curves in Fig. 2 show that a comparatively large percentage increase in hiding-power may be realized at the expense of small decrease in brightness. This point has already been alluded to in a previous paper⁶ where the conclusion was reached that the *ratio* of the percentage increase in hiding-power to the percentage decrease in brightness equalled four. In light of the present work, it becomes necessary to qualify this statement more rigorously, for it is evident that this ratio is dependent upon the brightness range used in the calculations. Furthermore, this ratio decreases steadily as the brightness decreases. For infinitesimal changes in brightness, the value of the above ratio (α) is as follows:

Brightness.	α	
90%	9	(i.e., the hiding-power increases, relatively, 9 per cent. as a result of decreasing the brightness, relatively, 1 per cent.)
85	5.7	
80	4.0	
75	3.0	
70	2.3	

Since all curves in Fig. 2 pass through the 0 – 100 point, these values of α apply quite generally to all white paints studied.

⁶ *Proc. Am. Soc. Testing Mat.*, 1920

(The advantage of making the initial brightness of the paint as great as possible is obvious.) If now, we make finite rather than infinitesimal changes in brightness, the value of α will depend upon the range of brightness used in the calculations. If we limit ourselves to the range within which most paints lie, *i.e.*, brightness 75 per cent. to 83 per cent., we find that, for this interval $\alpha = 5$. Possibly a more convenient form is that suggested by Dr. J. E. Booge, namely, the percentage increase in hiding-power per 1 per cent. (absolute) decrease in brightness. For the interval brightness 75 per cent. to 83 per cent. this ratio is very closely equal to 6.0. (This means that if we decrease the brightness from 80 per cent. to 79 per cent., a 6 per cent. increase in hiding-power is realized.)

The method of treating this problem, free from all uncertainty, depends upon the deduction of a formula which makes possible a calculation of the hiding-power at any brightness > 70 per cent. The curves in Figs. 2 and 3 are represented by the equation

$$y = -mx + a$$

making the following substitutions:

$y = H_B$ which is the hiding-power at any desired brightness $B > 70$ per cent.

$x = B$ which is the brightness corresponding to H_B .

$a = H_0$ which is the hiding-power at zero brightness (extrapolated).

$m = \frac{\Delta H}{\Delta B}$ which is the slope of the curve (Fig. 2 or 3)

then we have:

$$H_B = H_0 - \frac{\Delta H}{\Delta B} B$$

The operation of this formula may, perhaps, best be illustrated by citing a specific illustration: Let it be desired to calculate the hiding-power H_B of a lithopone paint (Fig. 3) reduced to the brightness 77.1 per cent. of white lead paint (curve 2). Here

$$B = 77.1$$

$$H_0 = 1502 \text{ sq. ft. per gal.}$$

$$\frac{\Delta H}{\Delta B} = 15$$

$$\therefore H_B = 1502 - (15 \times 77.1) = 346 \text{ sq. ft. per gal.}$$

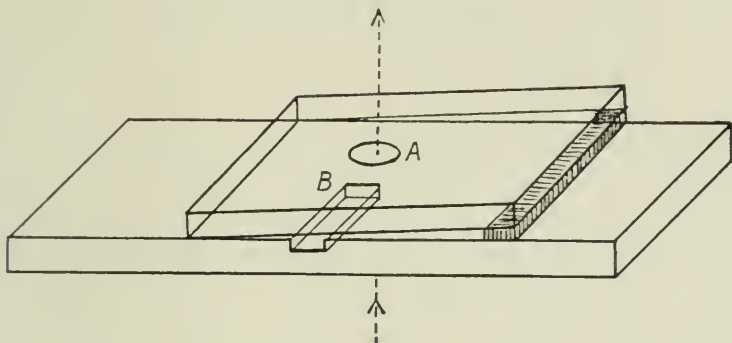
This result agrees with that obtained from the curves, directly.

It was next deemed of interest to investigate the relation between the so-called "opacity" and hiding-power. A white

pigment owes its brightness to a multiplicity of reflecting surfaces which return the incident light. As a result of such return, the intensity of the transmitted light is weakened and opacity, or better, "pseudo-absorption" develops. This may be illustrated by means of a clear piece of mica which, after having been glowd in a bunsen flame, appears almost white by reflection and black by transmission. Failure to transmit is not due to a change in the transparency of the material but to the numerous cleavage planes which now reflect the light.

In the event that all paints showed the same opacity at complete hiding, it would be possible to construct a modified

FIG. 4.



cryptometer of great sensitiveness. Anticipating subsequent results, it may be stated that these hopes were not realized. It was shown, however, that opacity, like tinctorial strength,⁷ is not a quantitative measure of true hiding-power.

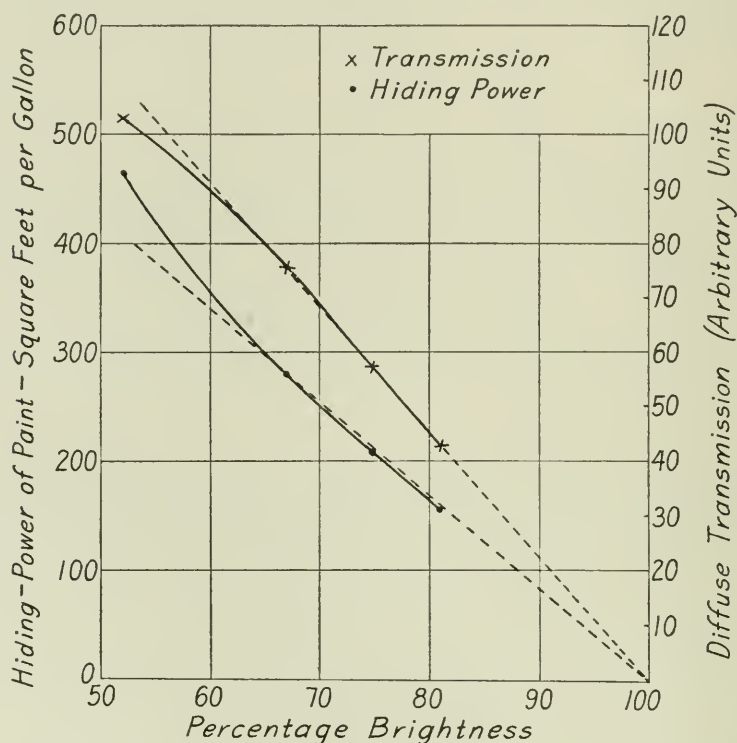
For purposes of this study, a special cryptometer was constructed. The usual deep groove was allowed to extend only half across the lower plate and a circular window *A* (Fig. 4), whose centre was in line with edge *B* was cut in the black coating covering the lower surface of the plate (made of clear plate glass). A given paint mixture was then applied to the cryptometer and the usual adjustment for disappearance of the edge *B* was made. Without disturbing this adjustment, an intense beam of white light was allowed to enter the window *A* and to pass through that portion of the paint film which had a thickness just sufficient for complete hiding. Photometric measurements of the ratio of the intensity of the emergent to the light incident upon film were subsequently carried out. The values recorded are purely

⁷ Hallett, *Proc. Am. Soc. Testing Mat.*, 1922.

relative and are termed "diffuse transmissions." Obviously, they are the reciprocals of "opacities." The following curves (Fig. 5) apply to a mixture of zinc oxide and linseed oil—rubbed down with small quantities of bone-black. The brightness of these mixtures is plotted against both hiding-power and diffuse transmission.

These curves reveal the surprising result that, as bone-black is added, both *hiding-power* and *transmission* increase. In other

FIG. 5.

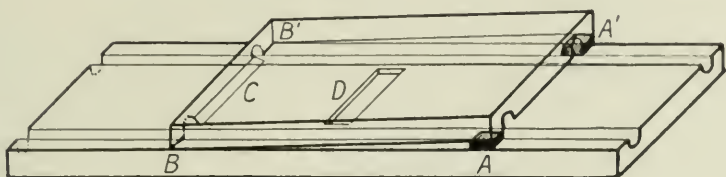


words, a film of gray paint, which is just sufficiently thick to "hide," shows greater transparency than a film of white paint which, likewise, is just sufficiently thick to "hide." Curiously enough, the straight-line extrapolation of the transmission curve also passes through the 0 - 100 point and thus allows us to draw the entirely logical conclusion that a paint showing 100 per cent. brightness is entirely opaque.

While the immediate prospects of realizing a cryptometer which would reveal very small differences in hiding-power were not realized, it was found possible to overcome a difficulty which

is met in practice when paints, containing barytes and other coarse particles, are being investigated. These coarse particles get under the areas of contact of the two cryptometer plates—hence, if the pressure on the top plate is only moderate, the coarse particles are neither crushed nor forced out and, as a result, the cryptometer reading is too low. If, on the other hand, sufficiently great pressure is exerted, the top plate is distorted and readings which are too high are obtained. Furthermore, such pressure in

FIG. 6.



conjunction with sliding motion causes a grinding action which, in time, occasions a change in the wedge-constant. These difficulties have been overcome entirely by cutting deep longitudinal grooves into both upper and lower plates (Fig. 6).

The usual metallic strip attached to the top plate is replaced by two small metallic squares at *A* and *A'*; again, the glass in the central area at *C* is cut away for a distance of 5 mm. When this plate is laid upon the lower one, contact is made only on the outer, narrow strips at *AA'* and *BB'*. Upon filling in the ends of the transverse groove, *D*, it is found that, when paint is applied to the area between the longitudinal grooves, the upper plate may be moved back and forth many times without dragging paint to the outer strips along which the plates are in contact. Needless to say, no pressure other than the weight of the top plate is now necessary. Very consistent results are obtained as a result of these modifications.

A further refinement has been introduced in obtaining the wedge-constant. Through the use of monochromatic light, interference fringes, running parallel to the edge *D*, may be formed in the wedge-shaped air film between the two plates. By mounting the cryptometer on a dividing-engine and counting, under the microscope, the number of fringes lying in a known distance, the wedge-constant may be determined as accurately as we please—certainly better than a few tenths of 1 per cent.

SUMMARY.

1. A straight-line extrapolation of the brightness-hiding-power curve (from 70 per cent. brightness upwards) of a white paint, grayed with bone-black, passes through the point: 100 per cent. brightness, zero hiding-power. Comparisons of the hiding-powers of different paints and pigments at equal brightness may be carried out.

2. For the brightness range 75 per cent. to 83 per cent., the ratio of the percentage increase in hiding-power, to the percentage decrease in brightness = 5.0 for all white paints.

3. At "complete hiding" a gray paint film is much more transparent (less opaque) than a corresponding white film. Caution must be exercised in drawing conclusions relative to hiding-power from opacity measurements.

4. A modified cryptometer is described. The paint is prevented entirely from working under the areas of contact of the two plates.

This investigation was begun at the Experimental Station of the E. I. du Pont de Nemours Company, and was completed at the Johns Hopkins University.

Reverberation in Auditoriums. F. R. WATSON. (*Phys. Rev.*, Feb., 1923.)—The time it takes a sound in an auditorium to die away is approximately in proportion to the cube root of the volume of the room, while for the best effect the intensity of the sound generated should be in proportion to the square of the cube root of the same volume.
G. F. S.

The Production of Artificial Vowel Sounds. SIR R. A. S. PAGET. (*Proc. Royal Soc.*, A719.)—In some manner we can usually understand what people say, whether they are children or adults, men or women, native or foreigners. We can recognize the same word though the sounds which we actually hear and translate into that word differ greatly according to the lips from which they issue. The author has been listening to the breathed vowel sounds of his own voice and has been analyzing them into two component notes of different pitches, due to resonance of the oral cavity. Sometimes these components are close together in pitch as in the "a" of calm and the "o" of not, or again they may be several octaves apart as is the case with the vowel sound of eat. The author has achieved considerable success in producing vowels with strangely shaped plasticine models to which artificial larynxes were attached, and he finds that good results come with two resonators placed either in series or in parallel.
G. F. S.

ON UNIVERSAL AND OTHER CONSTANTS.*

BY

ENOCH KARRER.

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FROM a certain philosophic viewpoint the universe may be defined as a flux of things. On account of interactions giving rise to sensations, we feel that we may know something as to what or how the things do. As to what or how the things are we have no such immediate knowledge, but, by additional neural processes we make abstractions from our sensations and build up an analysis of what is this flux of things. It happens that, for most of us, most of the time a mere naming of the thing is a sufficient answer to the query: What is it? On close scrutiny we find that the thing named is, at any instant, a complex of stimuli that may give rise to a complex of sensations. It is this complex of sensations that we analyze from moment to moment to arrive at a knowledge of the thing in detail. The analysis leads to facts far removed from sensations, and onto paths quite inaccessible to sensations. Sensations are, after all, of a gross and practical nature. At the same time the conclusion which is arrived at in the practical world that the thing "exists" irrespective of the sensations is as inevitable as the sensations† themselves. For, although the abstractions leading to the concept and the naming of the thing seem to be the result of, or built up of sensations, we find that this process has already taken place when we become aware. It has indeed perhaps to a large extent taken place in

* Communicated by the Author.

† The analytic processes go so far as to lead to an inversion of the simple sequence narrated here. We formulate pictures of parts of the universe, and then, if they appear logically congruent, we strive to show that conditions can be found or defined under which our sensations or experience will be in accord with the pictures. The fact of the matter is that we have no hint as to what part consciousness or "self" plays in this interpretation of the flux of things. In all the physical sciences this is ignored, as I have done in presenting this viewpoint of the constants of nature. I cannot refrain from quoting one of my psychological colleagues who puts it thus: That the universe is such that it explains all of the constants, rather than that the constants explain the universe as the physicist would have it.

the animal nervous system, and merely awaits to be taken over into consciousness as exists in man.¹ Since it is by analysis that we know what the thing is, it may be said in a more or less paradoxical and misleading manner that things are what we think they are. Of course, it is all important what kind of thinking it is. Just in the same way, however, that in the sensations of sight, it is important what kind of seeing is done. A great practical difference is that the part of our nervous system that does the elemental seeing is more restrained and therefore less erratic than the part that does the thinking.

The fact then that we know things "to be," and the fact that we know about them through the sensations are coaxiomic.

There appears to be no limit to the extent of this analysis of the flux of things about us. The most essential elements of sensorial import that enter into it are the metrical aspects of time and of three dimensional space. It is a fundamental feature, too, that we find strata as it were, in the flux of things that flux differently relatively to each other. For we need to set surveyor's stakes or benchmarks into some stratum or other as reference points along the paths of our analysis. These benchmarks are the constants of science. Their constancy is only a relative matter. It suffices that it extend over sufficiently long intervals of time and space to allow us "breathing spells." As our experience and analysis proceeds we analyze the constants in terms of others that are more constant. There is probably no constant in the absolute sense that it is ordinarily looked upon in practice.

¹ We can find material suggestive of what I mean here in many cases of animal behavior, where a more or less complicated and coördinated series of reactions are involved. Take, for example, instances from among the wasps, the "mud daubers," which I have had many hours of pleasure in observing. Proper stimulus complexes lead them to form and carry mud pellets a great distance; and further stimulus complexes lead them to place the pellets systematically to form a housing, into which eggs are deposited in an orderly fashion, together with an ample supply of spiders well selected and preserved by inoculation to nourish the future larvæ. Errors may occur anywhere in these complicated performances, I have observed, for instance, that a wasp may carry mud for hours before it begins to deposit the pellets systematically in the same place. We have here certainly all the nervous substrata for such mental states that I am referring to. All that is required outside of perhaps more associational elements, is a cloak of consciousness or awareness, if it does not already exist.

Constants arrived at analytically and experimentally are the milestones of progress in our interpretation of the universe. It would seem therefore that, as data are piled up and theories are formed and reformed, a surveying glance over these constants properly classified, would give some assistance and pleasure. A simple classification is to call the constants independent² universal constants that apply to all matter, all electricity and to all processes, and from which all others may be derived; and to call others derived universal constants that are independent of materials and derivable from the first. A third class of constants are reference points by definition or experiment. A fourth class are the conversion factors³ stating the relation between different units, and systems of units, and between different reference points. The fifth and largest class takes in the constants describing the properties of materials, and of instruments or mechanisms.

The purpose of the present note is chiefly to dwell upon a detailed classification of the independent universal constants, but I shall digress to give examples of the various groups in the following tables.⁴ Those of the universal constants in groups 1 and 2 that are obtainable by independent measurement are marked with asterisks; those determinable with an accuracy sufficient to

² By independent is meant that the constants are not analytically functions of each other so far as is now known. How they may be related is shown by the constants derived from them. A better way of stating the fact is that all of the universal constants are interrelated in divers ways, but that a few of these relationships may be selected such that all others may be expressed in terms of them. The decision then as to which constants are independent rests upon one's viewpoint. See also footnote 11 below.

³ For the most part conversion factors other than unity are like erasures or, rather, like corrected connections between lines drawn from two directions that do not meet as intended, on the scroll upon which our picture of the universe is being depicted.

⁴ The constants which I give here are selected from a list and classification of constants that were reported to the National Research Council through Dr. E. P. Hyde, Director of Research, by a committee consisting of Drs. E. Q. Adams, W. E. Forsythe, A. G. Worthing and E. Karrer. I am departing somewhat from that classification both in the designation and in the number of groups. The constants given in group 1, however, are taken in their entirety from the committee report. Although the present stimulus for this communication has largely been the committee work, yet I have entertained the idea for sometime of making some such contribution with the object of showing the proper place for certain concepts that have recently entered into the literature of photometry and illuminating engineering.

warrant their use in calculating others, including those with single asterisk, are indicated with double asterisk.

All numerical values are based upon the fundamental units: Centimetre, gram, second, degree (K.), $1/16$ of the atomic weight of oxygen, and the dielectric constant of free space; and, being illustrative merely, are given for the most part to two significant figures only.⁵

1. Independent Universal Constants.

Symbol.	Numerical value.	Name.
c	$**3.0 \times 10^{10}$ cm. sec. ⁻¹	Velocity of light in free space.
γ	$**6.66 \times 10^8$ g. ⁻¹ cm. ⁺³ sec. ⁻²	Newtonian gravitational constant.
e	$**4.8 \times 10^{-10}$ c. g. s., e. s. u.	Electronic charge.
m_o	9.0×10^{-23} g.	Mass of isolated resting electron.
m_p	1.6×10^{-24} g.	Mass of proton (in heavy elements).
k	1.4×10^{-16} erg. p. °K.	Molecular gas constant, coefficient of Boltzman's entropy equation.
h	6.5×10^{-27} erg. sec.	Planck's constant, quantum of action.

2. Derived⁶ Universal Constants.

Symbol.	Formula.	Numerical value.	Name.
	e/m_o	$**5.4 \times 10^{17}$ e.s.u.g. ⁻¹	Bucherer constant.
	$e/m_o c$	$**1.8 \times 10^7$ e.m.u.g. ⁻¹	Bucherer constant.
	ch/e	$**4.2 \times 10^{-7}$ erg. cm. e.s.u. ⁻¹	Photoelectric quantum.
	k/e	$*2.9 \times 10^{-7}$ erg. per e.s.u.°K.	Thermoelectric quantum.
e_a	$2e_1$	$*9.5 \times 10^{-10}$ c.g.s.e.s.u.	Charge on α -particle.
N_∞	$\frac{2\pi m_o e^4}{k^2 c h^3}$	$*1.1 \times 10^5$ cm. ⁻¹	Rydberg wave number (according to Bohr).
c_2	ch/k	$**1.430$ cm. °K.	Second constant of Planck's radiation law.
σ	$\frac{2\pi^5 k^4}{15^2 h^3}$	$*5.7 \times 10^{-5}$ erg. cm. ⁻² sec. ⁻¹ °K. ⁻⁴	Stefan-Boltzman constant.
F	$10 Ne/c$	$**9.6 \times 10^4$ coulombs per mol.	Faraday's constant of electrolysis.
F_p	F/m_H	2.58×10^4 coulombs per mol. g. ⁻¹	Ditto for gram of hydrogen.
R	$Nk/10^7$	$\left\{ \begin{array}{l} **8.3 \text{ joules per mol. } ^\circ\text{K.} \\ 2.0 \text{ cal. per mol. } ^\circ\text{K.} \end{array} \right\}$	Molar gas constant.
$\lambda_m T$	$c_3/4.9651$	$*0.29$ cm. °K.	Constant Wien's displacement law.
N	$1/m_p$	$*6.1 \times 10^{23}$ g.	Number of molecules per gram molecule.
n		2.7×10^{19} cm. ⁻³	Loschmidt's number. Number of molecules in 1 c.c. NPT.
	$1/\mu$	$*9.0 \times 10^{20}$ cm. ² sec. ⁻²	Kinematic elasticity of ether.
c_1	$2\pi c^2 h$	3.7×10^{-5} erg. cm. ² sec. ⁻¹	First constant of Planck's radiation law.

⁵ The two underscored constants are among those referred to in the previous footnote.

⁶ How they are derived from the independent universal constants is indicated in the second column where the formulas are given.

Symbol.	Formula.	Numerical value.	Name.
ν_{∞}	$cN\alpha$	$3.3 \times 10^{16} \text{ sec.}^{-1}$	Rydberg's fundamental frequency.
α	$2\pi e^2/\hbar c$	$5.30 \times 10^{-10} \text{ sec.}^{-1}$	Bohr's constant for fine structure of spectral lines.
a_1	$2e^2/3m_0c^2$	$1.9 \times 10^{-13} \text{ cm.}$	Radius of Lorentz surface-charged electron at rest.
a_2	$4e^2/5m_0c^2$	$2.2 \times 10^{-13} \text{ cm.}$	Radius of Lorentz volume-charged electron at rest.
ϵ	$3/2k$	$2.1 \times 10^{-16} \text{ erg. per } ^\circ\text{K.}$	Temperature coefficient of energy of monatomic gas molecule.
a	$4\sigma/c$	$7.6 \times 10^{-15} \text{ erg. cm.}^{-3} \text{ } ^\circ\text{K.}^{-4}$	Coefficient of Stefan-Boltzman law for density of radiant energy.
m_H	$1.008 \times m_p$	$1.7 \times 10^{-24} \text{ g}$	Mass of resting neutral hydrogen atom.
m_{He}	$3.99 \times m_p$	$6.6 \times 10^{-24} \text{ g}$	Mass of resting neutral helium atom.

3. Reference Points.

(By definition and experiment.)

Symbol.	Numerical value.	Name or definition.
g	$980 \text{ cm. sec.}^{-2}$	Acceleration of gravity at sea level and 45° latitude.
T_0	$273.13 \text{ } ^\circ\text{K.}$	Freezing point of water (absolute centigrade scale).
V_0	$22.4 \text{ litres in mol.}$	Volume of gram molecule at NPT (normal pressure and temperature).
c_v	$3R = 6.0 \text{ cal. per mol. } ^\circ\text{K.}$	Atomic heat of solids (Dulong and Petit).
d_c	$3.0 \times 10^{-9} \text{ cm.}$	Grating space of calcite.
λ_{cd}	$6438.47 \times 10^{-8} \text{ cm.}$	Wave-length cadmium red line in terms of which the meter has been measured

and many others, such as the magnetic permeability, the density and viscosity of air, etc.

4. Conversion Factors.

Symbol.	Numerical value.	Name or definition.
J	$4.2 \text{ joules per cal.}$	Ratio of joule to the mean calorie, thermo-mechanical conversion factor, mechanical equivalent of heat.
$1/P_m$	$0.00150 \text{ watts per lumen}$	Minimum ratio of watt to lumen ($\lambda = 556m\mu$), photo-mechanical conversion factor, mechanical equivalent of light. ⁷
P_m	$667 \text{ lumens per watt}$	Maximum ratio of lumen to watt, visibility ⁸ of light at $\lambda = 556m\mu$.

⁷ This last phrase has misleading historical connotation, and either of the first two are preferable to it. It gives to the factor the significance that the mechanical equivalent of heat once possessed but no longer retains. (See Buckingham, *Phil. Mag.*, p. 710, 1921.)

⁸ The nomenclature should be so adjusted in any one department of science that all duplicity of meanings is avoided. This is not true with the word visibility in optics. In addition to the above use there is the visibility of objects and of interference fringes. For the latter case we have the well-known visibility curves. (See note 9.)

5. *Constants of Materials and of Instruments.*

A. Constants of Instruments Used in

1. Physics.

a. Mechanics.

Statics.

Dynamics.

Sound and acoustics.

Heat and thermodynamics.

b. Electromagnetics.

Electrostatics.

Electrodynamics.

Radiation.⁹

Photic¹⁰ radiation.

1.5×10^{-9} ergs. sec.⁻¹ threshold of dark adapted eye.

0.006 Weber's constant at ordinary brightness.

Ultra-photic radiation.

Gamma rays.

Röntgen rays.

Ultra-violet.

Infra-photic radiation.

Infra-red.

"Rest strahlen."

Hertz radiation.

Wireless waves, and longer. }

Extra-photic radiation.

2. Physical chemistry.

3. Chemistry.

4. Engineering.

5. Biology.

etc.

B. Constants of Materials.

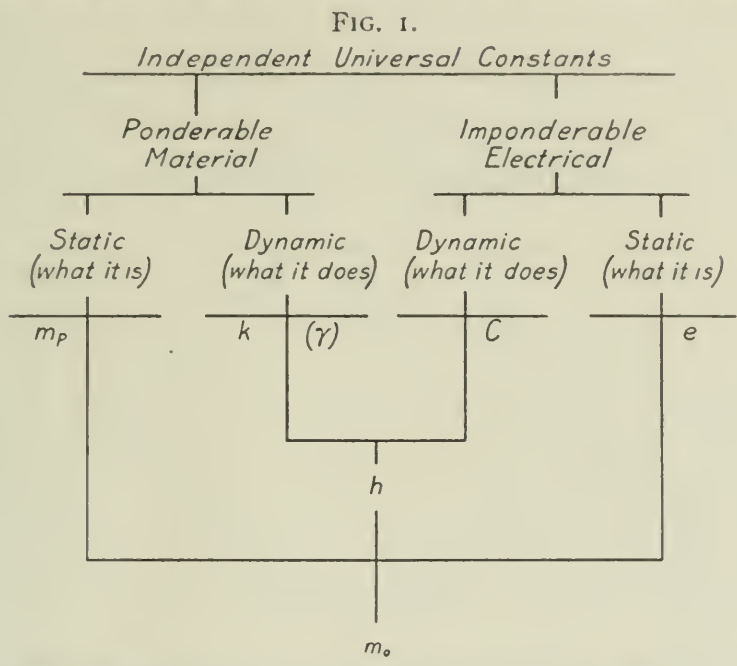
Subdivisions and subheads as suggested in A.

Returning to the independent universal constants, it is seen that seven of them may be selected such that all others may be expressed in terms of them. The seven given in group 1 appear to be the simplest analytically. It is interesting that the number is small—seven in the present state of knowledge and possibly

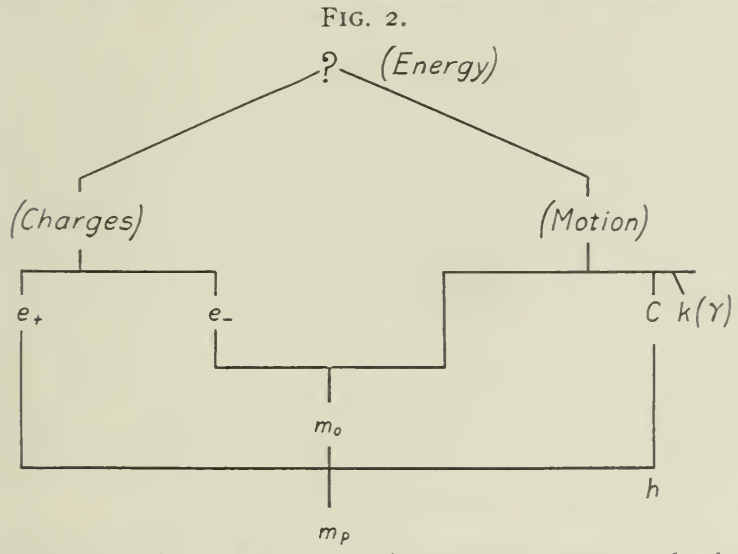
⁹ To avoid entirely the objections noted in footnote 8, the word photic is used instead of visible. The Latin prefixes are preferred to the Greek prefixes (hyper and hypo), because one of the latter is already attached in the word hypo-phonic (musical term) to a meaning different from that desired here. The Latin prefixes allow terminology in acoustics similar to that suggested here for optics. From one viewpoint optics and acoustics are subdivision of radiation.

¹⁰ The examples given here would of course fall under proper subheads. They are inserted to show that the sense organs may be treated as instruments in so far as they have constants that are of practical importance to any particular science, such as the eye has in photometry.

only six, as will be indicated later.¹¹ These seven may be further superficially classified according as to whether they pertain to ponderable matter or to electricity. The constants m_p , γ and k



A chart suggesting a classification of and the relationships between the seven independent constants, based upon the notions *ponderability* and *imponderability*.

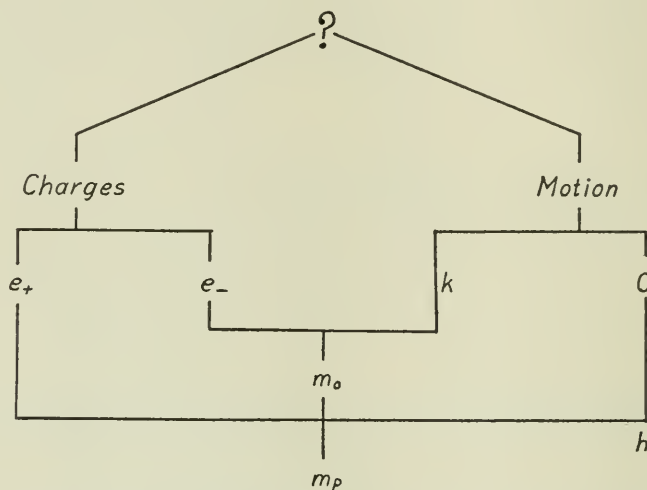


A chart suggesting relationships between the seven independent constants, under the two notions of *charges* and *motion*. For the symmetry of this chart see Fig. 3.

¹¹ The number of fundamental units of measure is less than seven, so that on further analysis there must appear a lesser number of independent universal constants. Since the writing of this paper there has come to my attention an interesting paper by Lunn (*Phys. Rev.*, July, 1922) who gives considerations bearing upon this point.

distinctly are those pertaining to gross ponderable matter, while e and c are those belonging clearly to the electrical. There are left then m_0 and h which are not so easily disposed of in this classification, but hold rather an intermediate position; since m_0 is a property of the electron (e) but has ponderability, and h is a factor somewhat like c pertaining to electromagnetic radiation but in fact is always associated with an m_p . It may be noted, however, that this classification brings out the fact that these

FIG. 3.



A symmetrical chart suggesting the relationships between the seven independent constants classified under the two categories, *charges* and *motion*.

constants occur in pairs, each of which contains a static and a dynamic factor. For example, m_p and k (or γ) are a pair, as are also e and c , leaving m_0 and h . From a philosophic viewpoint it might be expected that the independent constants may occur in pairs, describing the properties of things in a way to answer the two queries: "What is it?" and "how it does?" This duality has already been hinted at in the introductory words. Our answer to the latter query may be traced back more or less directly to the sensations. The answer to the former is arrived at, even in its simplest aspect, only after some analysis of the sensations. Similarly, it might be expected that where several constants occur in reply to either query, only one would stand out as preëminent, and the others as derivable from or as incidental to it. This may be the case with γ or k , and since most attempts at theories of gravitation strive to give γ in terms of other constants, I have subordinated γ rather than k . The essence of the whole philosophy

of the conservation of energy, in so far as it has had historical significance in heat, is embodied in k . The classification of the independent constants has then a duality at all points. In Fig. 1 given below to represent these ideas, h and m_0 are put in an intermediary place as might be done if they are thought of as the pair of constants resulting from the interaction of ponderable matter and electricity. The diagram in Fig. 1 is not satisfactory. It is not well balanced in many respects. This classification is one that may be made if the equivalence between electromagnetic inertia and gravitational inertia is entirely ignored. The latest trends in physics do not allow a division of subject matter into the "electrical" and the "ponderable." In another attempt represented in Fig. 2, I have borne in mind that present-day analysis of physical phenomena emphasizes two things, motion and electrical charges. Further, if one considers c the motion constant where velocities of great or limiting magnitude enter, and k as typical of motion constants where velocities of small magnitude enter, then k might appropriately be inserted to antecede m_0 as in Fig. 3, which becomes a more symmetrical one. Our ordinary concepts of matter and electricity are associated with the central and left portions respectively, while those of radiation are associated with the extreme right portion of the chart.

A New Industrial Factor, the Utilization of the Calories Furnished by Hot Springs. J. DYBOWSKI. (*Comptes Rendus*, March 12, 1923.)—Since the destruction of the mines of coal in and about Lens by the Germans, France has been seeking to find means of utilizing to the full any sources of energy she may have. Winds, tides and rivers have been laid under contribution to replace in some measure the loss of coal due to the invaders. Now it is the turn of the hot springs to be harnessed in the service of man. The low temperature of the waters imposes very evident limits on the use to which they may be applied. They readily lend themselves to domestic uses or to bathing installations. In the distinctly industrial field is the heating of hothouses for the raising of early vegetables. Such an experiment has been made in the southwestern part of France in the department of Landes at Prechacq.

Let there be a spring yielding 50 cubic metres per hour of water at 62° C. If this after utilization is discharged at 25° C. it will liberate in an hour 1,850,000 large calories. The author reckons this to be equivalent to the burning of 1057 kg. of coal per hour, or of about 25 tons per day. The waste of heat from the water should not exceed 10 per cent. in a well-organized plant.

Not all hot springs can be thus utilized. If the water be below 60° C., or if it be too strongly impregnated with minerals or gases, it can not be used to advantage. Of course the climate in the region of the spring makes much difference. A low temperature will cause great loss of heat. Besides this the place where the hothouses are can not be too far from the spring owing to losses in transmission. In the plant at Prechacq the water issues from borings at a temperature of 63° and is led 2.3 km. (1.8 miles) to a series of greenhouses, each covering a quarter of a hectare (half an acre). The total area warmed is 10 hectares, 23 acres.

G. F. S.

Velocity of Sound in Sea Water. E. B. STEPHENSON. (*Phys. Rev.*, Feb., 1923.)—It is illuminating to compare the experimental methods here used with those employed by Colladon and Sturm in their classical determination of the velocity of sound in lake water in 1827. The experiments here described were conducted in Block Island Sound in January, 1922. The method "consisted in electrically detonating a .5 kg. bomb of TNT at a depth of 8 to 10 metres, and simultaneously sending a radio signal at a distance of approximately 18,000 metres from shore. The sound through water was received by a series of five hydrophones . . . connected by cable to a central shore station. . . . A string galvanometer with six strings, a tuning fork controlled timing device, and a photographic recording camera, gave a record of the vibrations of the strings with transverse timing lines at .01-second intervals." It was possible to read the intervals between the instant of explosion and the time of the arrival of the sound wave at the hydrophone to .001 second.

The location of the hydrophones was determined at the time they were placed in position by observations from the shore. "The location of the bomb at the instant of firing was determined by observations on the target (attached to it) from three shore stations on two base lines about 10,000 metres each in length." The chief difficulty in the work lay in finding a time when all the factors were in favorable conjunction. "This was particularly true of the visibility, since it was necessary to observe the target simultaneously from three observation stations at distances of approximately 16 kilometres, and to read its angular position to $.01^{\circ}$."

The final average of the velocity is 1453.3 metres per second. The temperature of the water was -3° C. and its salinity 3.35 per cent.

G. F. S.

Sound Transmission of Sawdust Concrete. D. L. RICH and C. R. BROWN. (*Phys. Rev.*, Feb., 1923.)—Slabs of concrete containing sawdust were cast with the thought that the resulting material would be light in weight and would in addition be a poor conductor of sound on account of its porosity. Strange to relate, the slabs with a high sawdust content proved to transmit sound better than solid concrete itself.

G. F. S.

THE SENSE OF VERTICALITY AND ITS APPLICATION TO LIGHTHOUSE WORK.*

BY

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WHEREVER navigators have to lead boats through difficult waters, means to show the navigable channel have to be provided for. During the day, natural marks in the landscape have been for centuries, and are still, to a great extent, the only guides used by mariners acquainted with the locality. In much frequented waters, however, and at night, more reliable aids had to be installed. Floating bodies, moored at the proper place, are the usual means of marking a channel when the latter is at all crooked or exceedingly narrow; the design of buoys has been wonderfully improved in the last thirty years and to-day light buoys, bell buoys, whistling buoys, buoys with submarine signal attachment and others are used all over the world. But this method of marking navigable waters is expensive and when the channel is straight over a reasonable distance and is free from obstacles, it has been found cheaper, and most often more convenient, to mark its axis by means of two stations, generally high towers provided with powerful lights and placed at one end.

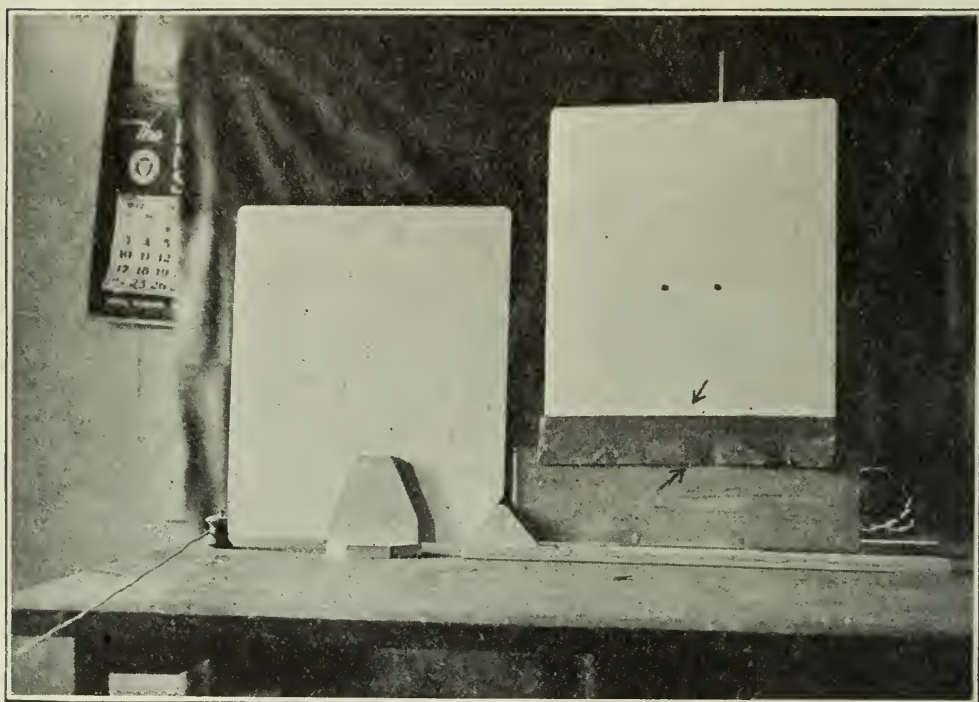
Boats follow the channel as long as they keep in line with the two marks. In practice, however, the mariners cannot use these marks as a surveyor would two rods to run a straight line; the latter conceals the farther rod with the nearer one and, from time to time, ascertains that he has both still in line by stepping on either side and thus "opening" the rods; the mariner, having no such freedom of motion, must at all times see both lights. To secure this result the back tower is considerably higher than the front one, their respective heights being calculated so that from the farthest point of visibility the two lights appear still as distinct, *i.e.*, subtend an angle of not less than four minutes according to the most generally accepted rule. Then, of course, the problem facing the mariner is no more that of placing two rods in line

* Communicated by the Author.

with his eye, but to put two points on a same vertical; and to what extent our "sense of verticality" can be relied upon is still an open question.

In 1864, Léonce Reynaud, in his "Mémoire sur l'Eclairage et le Balisage des Côtes de France," suggested as a limit for the possible error the quarter of the angular distance of both lights increased by four minutes. This rule errs obviously on the safe side and would necessitate very expensive ranges, the more

FIG. I.



so since L. Reynaud recommended at the same time a minimum angular distance of from eight to fifteen minutes, according to the power of the lights.

In 1902 (*Ann. P. Ch.*), M. de Joly made a new study of the question and found the error in the estimation of verticality "nearly negligible." This, however, does not offer any safe rule for the calculation of the distance between the two lights of a range, and the usual practice among lighthouse engineers has been to take as the minimum of the distance of the two lights a set fraction of the useful length of the range—generally from one-tenth to one-twelfth.

This method is obviously unsatisfactory since it would lead to give the same sensitivity to two ranges used to mark, say, one a channel 400 feet wide, and the other, a pass half a mile large, if in both cases the point of maximum danger happened to be located at the same distance from the front light. Safe and reasonable results cannot be obtained unless the angular distance measuring the "opening" of the two lights at the edge of the channel is introduced in the calculation. This angular distance should be such that the non-verticality of the line passing through the two lights could then not be questioned.

In order to ascertain what could be considered a safe limit beyond which the two lights should appear on two different verticals, the writer has endeavored to realize in the laboratory conditions somewhat similar to those of a range, and has measured the angular distance between the verticals passing through two very small lighted and movable points which observers had been requested to place on the same vertical line.

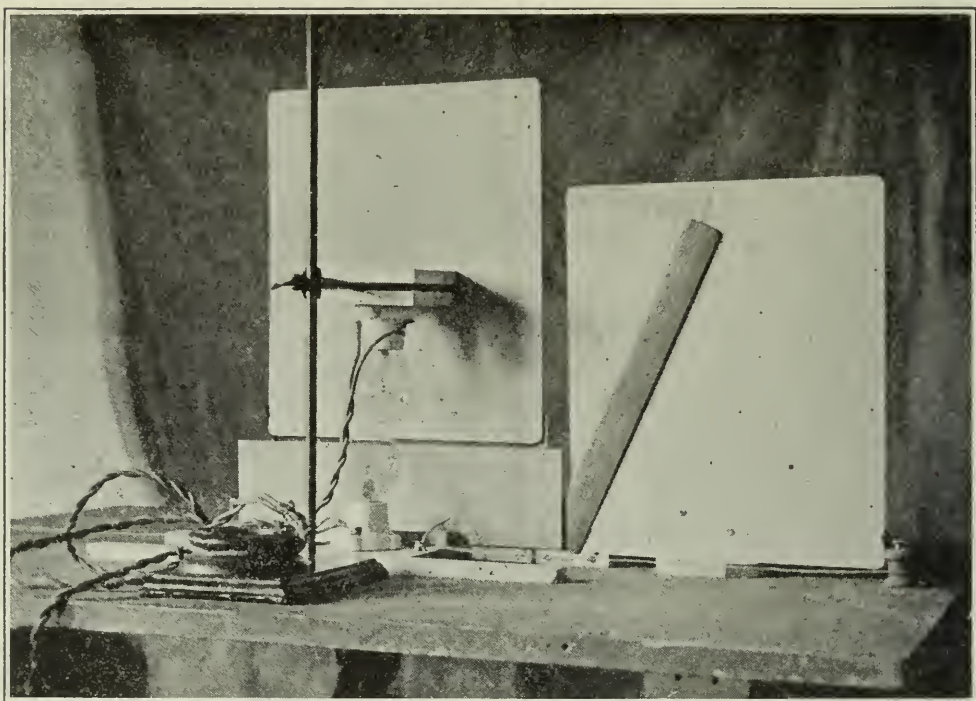
The Apparatus.—The apparatus consisted essentially of two electric lamps in front of which were placed screens with pin-holes, one each. The upper lamp was fixed, while the lower was mounted together with the screen on a carriage sliding between two parallel strips of wood and placed so that the two screens would be in the same plane. An endless string was fixed on the carriage, passed on idlers fixed to the table which carried the whole apparatus, and was attached to a drum placed in front of the observer; by this means, the latter, who was some thirty feet distant from the screens, could move the lower one to bring it to the position which, in his judgment, placed the two lighted pin-holes on the same vertical. The left end on the movable screen was abutting against a lever fitted with a needle which moved on a fixed dial, the latter having been empirically graduated to read small displacements ($1/50$ of an inch), and an assistant to the observer, placed on the light's side of the screens, read the position each time the observer declared himself satisfied that he had both pin-holes "in line."

The distance of the pin-holes was varied and, of course, it was found that the difficulty of correctly placing the lights increased after the angular distance passed a certain limit. Later the experiment was repeated with a sector of paper on which a black line had been drawn; when the line was heavy enough to be

very readily seen, it seemed that the observer experienced much less difficulty in determining the vertical than he did with the first arrangement; the line, however, had to be comparatively long and subtended an angle of 2° .

Results.—The most comprehensive series of tests was made with the pin-holes at an angular distance of $0^\circ 22'$ which corresponds for two range lights seen at a distance of two miles to a difference of level of some 75 feet, a difference of height very

FIG. 2.



rarely reached. The conditions in the rooms where the experiment was carried out made it advisable not to try a lesser angular distance and since other observations showed that the sensitiveness of the readings decreased when the angular distance of the lights increased, one would seem justified in considering the results obtained as erring on the safe side.

In this series of tests, eleven observers, of very mixed training and ability, were requested to take readings, six for each observer. The results are given in Table I.

Five of the observers were obviously quite better than the others. Taking the average and the maxima in each case, we obtain the following results:

Average of 11 observers	$\left\{ \begin{array}{l} -26'' \\ 40'' \end{array} \right.$
Average of 5 best observers	$\left\{ \begin{array}{l} -20'' \\ 20'' \end{array} \right.$
Maximum of 11 observers	$\left\{ \begin{array}{l} -1' 14'' \\ 1' 46'' \end{array} \right.$
Maximum of 5 best observers	$\left\{ \begin{array}{l} -46'' \\ 56'' \end{array} \right.$

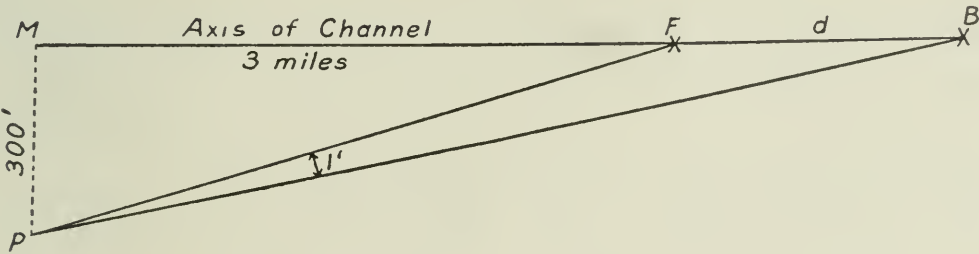
TABLE I.

Observers Readings	A	B	C	D	E	F	G	H	I	K	L
1	-18"	4"	-18"	32"	1' 14"	1' 46"	- 12"	22"	1' 38"	44"	1' 6"
2	- 8"	56"	-32"	- 4"	1' 0"	1' 50"	-1' 6"	-32"	32"	8"	56"
3	-22"	4"	-22"	-10"	- 6"	1' 6"	- 8"	18"	56"	-36"	22"
4	30"	26"	- 4"	30"	0	1' 24"	- 36"	-26"	56"	-10"	- 12"
5	22"	4"	-18"	-46"	46"	50"	-1' 14"	- 4"	1' 20"	-46"	22"
6	0	12"	-46"	- 8"	40"	50"	- 46"	-30"	1' 6"	-56"	6"
The five best	*	*	*	*	*						

In all the above the error of verticality is expressed by the angular distance between the actual position of the lower light and the one it should occupy.

As was to be expected, though the angular distance between the position of the lower light and that of the vertical passing

FIG. 3.



through the upper light increases when the angular distance of the two lights increases, the angle between the line joining the lights and the vertical decreases. Thus while this angle for the average error of the present series of tests was 2°, it was found to be half of that amount when the two lights subtended an angle of 1°30'.

Conclusion.—From the foregoing it would seem that an eye, trained as is that of the average mariner, should be able to detect readily for two lights a lack of verticality of less than $1'$, the angle being the angular distance between one of the lights and its proper position with respect to the other. In other words, the horizontal angle subtended by the verticals passing through the two lights seen from the edge of the safe channel should not be less than $1'$. Thus to mark a channel of 600 feet by a range, the front light of which would be located three miles up the channel, the minimum distance of the back light should be calculated as follows:

$$\begin{aligned} MP \tan \widehat{MPB} &= MF + FB \quad \text{with} \quad \widehat{FPM} = \text{verstan} \frac{MF}{MP} \\ \text{or} \quad FPM &= \text{verstan} \quad 60.8 = 89^\circ 3' 28'' \\ \widehat{MPB} &= 89^\circ 4' 28'' \\ 300 \times 61.90 - 18,240 &= d = \text{say } 330 \text{ feet} \end{aligned}$$

Distances thus obtained may still be somewhat empirical; they are, however, a nearer approximation to truth than those based on the old rule of a set fraction of the distance or similar ones, since they introduce in a rational way the main factor of the problem, *viz.*, the width of the channel at the distance where the danger is maximum.

Electrical Properties of a Flint Glass of Density 6.01. G. L. ADDENBROOKE. (*Phil. Mag.*, March, 1923.)—The approximate composition of this glass is SiO_2 , 22 per cent.; PbO , 78 per cent. "Judging by its density and composition, the density of natural silica being 2.61, fused silica 2.0, and lead 19.2 (?), it must contain over 30 per cent. by volume of metallic lead. It breaks easily, though hard. It softens and melts at a fairly low red-heat without showing any signs of blackening. That such a composition should be perfectly transparent and a high-class insulator is remarkable enough in itself." It has a refractive index for the D-line of 1.9201. When one forms Maxwell's ratio of the dielectric constant to the square of the refractive index the quotient comes out equal to 3.55. Other specimens of flint glass of different densities give for this ratio a series of values increasing as the density increases. For the flint glass of density 6.01 the dielectric constant is 13. "So far as I am aware this is not only the highest dielectric constant yet found for any glass, but it is the highest found for any material not of abnormal character and not complicated by the effects of absorption."

G. F. S.

MEASUREMENT OF THE WORK IN CRUSHING.*

BY

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THERE is a problem that has been handed down through the years, which remains a drag upon the milling industry of the present day. It is the problem of establishing the basis for measuring the work accomplished in crushing. Milling requires its solution, and needs assurance of the correctness of its grounds. Opinion, unsupported, is never to be accepted in the place of proven fact, and though the opinion of the industry has been fairly uniform, there has not been perfect agreement, owing to the want of expected mechanical demonstration with absolute precision. All mechanical demonstration is accompanied by interferences and limitations that obscure the real law. Though mechanical demonstrations of every detail of this operation are so abundant as to make the assembling of these details a matter of the merest common-sense, the lack of precision in the entire connected operation fails to satisfy those who would demand the last extreme in the offering of proof. In judgment here, as in every scientific judgment, from that of the conservation of energy to the theory that the earth is round, mechanical attainment requires the supplement of constructive reason to reveal the truth available in proven fact. Just as it would seem grievous to stay the progress of milling to demonstrate the law of gravitation, so it is wasteful to occupy a modern day with the discussion of this problem, if we may discover that we are agreed.

The evidence which appears awaiting to be recognized, and which is in common possession, is to the effect that the work of crushing is shown by a surface relation, and, other things being equal, is proportionate to the total of new surface produced by the operation. So long as any cloud rests upon the tentative truth of this assertion there will be impediment to advancement in milling practice, where power-consumption and utilization are important. Already the indecision has cost the industry too much.

* Communicated by the Author.

The attention of everyone who does not concur in these opinions is called to this matter. The desire is not to prolong the discussion, but to learn if the practice is not now able, with security, to end it, by reasons which appear to be irrefutable and final.

The point at issue is the interpretation of size-measurement in terms of work. People do not feel quite satisfied or convinced. The discussion flares up at times, as though it were a lingering flame on a field where once the fire of contention had been. But there has been no real contention. The recurrences are due, in most cases, to unmindfulness of published fact; but they leave the feeling of doubt in the general mind. If the reader is in agreement with the statement that the accomplishment in crushing is represented by the total of surface produced, he may proceed in the expectation of scientific progress and improvement. If, on the other hand, he believes otherwise, and has become entangled in the so-called "Kick's Law," there is need for him to go carefully into the matter, and, if necessary, to review the literature that throws light upon it.¹ The pity is that there is so little of

¹ Literature having direct bearing upon this subject is as follows:

"Lehrbuch der Aufbereitungskunde," P. Ritter von Rittinger, p. 20 *et seq.*, Berlin, 1867.

"Das Gesetz der Proportionalen Widerstände und Seine Anwendungen," Friedrich Kick, 1885, Leipzig, p. 1 *et seq.*

"Ore Dressing," R. H. Richards, 3, p. 1325 *et seq.*

"Economy of Power in Crushing Ore," E. A. Hersam, *Mining and Scientific Press*, 1907, 95, No. 20, p. 621.

"Grading Analyses and Their Application," H. Stadler, *Trans. Inst. of Min. and Met.*, 1909-10, 19, p. 478.

"Mechanical Efficiency in Crushing," Algernon Del Mar, *E. and M. Jr.*, 1912, 95, No. 24, p. 1129.

"The Crushing-Surface Diagram," A. O. Gates, *E. and M. Jr.*, 1913, 95, No. 21, p. 1039.

"The Work of Crushing," Arthur F. Taggart, *T. A. I. M. E.*, 1915, 48, p. 153.

"An Investigation on Rock Crushing Made at McGill University," John W. Bell, *Trans. Canadian Mining Institute*, 1916, 19, p. 151.

"Kick *vs.* Rittinger: An Experimental Investigation in Rock Crushing, Performed at Purdue University," A. O. Gates, *T. A. I. M. E.*, 1916, 52, p. 875.

"Kick *vs.* Rittinger: An Investigation of the Laws Governing Crushing in Ball Mills," E. A. Rolph, *Canadian Min. Jr.*, Aug. 18, 1922, p. 550.

substance to have occasioned the continuance of the discussion. When we shall have taken the brief time necessary to consider the matter, it is possible that we shall be agreed, and that the "Law of Kick," as offered to us, can be allowed to drop.

In order to know the efficiency of a crushing operation, we have to know, of course, the power applied and the power utilized. The quotient is the efficiency. In every judgment of efficiency, the consideration is limited to a definite case. The purpose is to determine something set apart, as a kind of rock, a kind of machine, a way of crushing. Whatever the quantities are that are used, or the manner in which the work is done, or the kind of appliance, the conditions have to be known. These can be described. They are uniform in all similar cases, and being held constant, may be eliminated from consideration without the requirement of a numerical assignment of values to them. They are the constant conditions. The choice of units does not matter.

There are, however, two considerations that are fundamental, which cannot be explained away by the manner of doing the work, nor by the hardness of the rock, nor the crudeness of the appliance. They are the real and fundamental variables that enter the calculation of efficiency. The one relates to the useful effect, and measures it, the other refers to the valuable power, and records it. It is suitable to call the first *accomplishment*, and the second *expenditure*.

Efficiency does not enter the consideration of accomplishment until some standard of accomplishment is known in terms of expenditure. Having this, it is possible to see efficiency as a ratio between the accomplishment in the specific case and that of absolute practice. Efficiency then, being a ratio, may be expressed in percentage, upon multiplying the ratio by one hundred. The units that enter it are combined units of accomplishment and expenditure. Such units are: The degree of fineness of the product, the horsepower, or, in fact, units of any other chosen kind capable of conversion. Being in ratio, they do not affect the results by their nature, but rather only by their relative magnitude, but in representation they must be truly expressive of actual expenditure and of real accomplishment.

In this ratio, we find no escape from the requirement of a numerical expression to show the accomplishment as well as the expenditure. Unless we know what the accomplishment is, and

can agree upon it, we cannot discuss efficiency, nor can we make any real scientific progress in matters that relate to efficiency. Having this numerical expression, we can take the highest value, or ratio, that was ever known, as obtained from the best work that was ever done, to be the temporary standard of efficiency. Such a standard held before us as ideal suffices while there is no other basis, and gives us the beginning of scientific comparison; but without the measurement of accomplishment, we are deprived of even this. It is clear that it is necessary to obtain, in numerical form, the expression of accomplishment in crushing, or of the degrees of accomplishment.

Rock that has been through a crusher, unquestionably, is changed in appearance. It is changed, possibly, in many ways that we do not see. It may be hot from friction, or bent by deformation, or under strain. The purpose that we had was to crush it. The effect that we got was this accomplishment and something more; but the accomplishment that we would measure is the crushing done, and nothing else. While it is easy to see, upon examining the rock, that something happened, difficulty arises when we undertake to judge the desired result, to exclude from it the useless things that happened, and to assign to it work-units. We must find the inherent quality that represents the desired effect, and measure it. We must examine the differences so closely as to be able to state the extent of the benefit. There is required then something which may guide us in excluding from the unit of accomplishment all the varying, opposing influences, and to rate such influences not as profit but as loss.

In judging the crushing of rock we encounter great complexity that comes from the comparison of dissimilar things. The one purpose is to make the rock fine. The measurement of work done is, therefore, a measurement of fineness. If anything other than producing fineness was done, it was done to no purpose. All else is outside the consideration, and is likened to resistance or to waste. The measurement of what was done is the measurement of the fineness. We are compelled to state what fineness means, and to express the degree of it. It must represent the total of accomplishment, based upon the total reduction in the size of all the components of the material as represented in all of the variously sized constituents of the product.

It is necessary, now, to see that our perception of the size

of anything relates to various dimensional attributes, of which the volume is only one. We are justified in representing size in any of these aspects, according to the manner in which the object functions, but in every case must affix the conditions, and affirm the degree. The size of a solid object, under conditions of similarity of shape, therefore, is truly represented by a dimension, by the surface, or by the cubical content. Each aspect is a consideration apart. Each may be represented by another upon affixing the corresponding index, but when converted, the conditions are distinct. The simple requirement here, for reasons that we shall see, is to represent the size of particles in terms of the surface of such particles.

The surface significance of size is necessary, in crushing or grinding, because of the fact that the rupture of solid substance, while it changes both the volume and dimension of the separate pieces, arrives at this result by severing the cohering molecules that lie along a plane. New exposure, or new surface is made by driving the flaw, fracture, or cleft, into an interior, and applying such energy as to produce this new surface in opposition to the force of solid cohesion. Molecular disturbance varying with the hardness and other qualities of the rock necessarily occurs beneath the surface, for the surface is but the ideal of area without substance. But the disturbance, which is represented by the alteration of the surface, is an exchange of energy in the adjustment of molecular forces that are affected by the surface to meet the requirements of surface structure. Being thus of the constant depth, required by nature of the substance, the surface alteration, so far as this may include the idea of volume, is proportionate to the surface. Such work, whether of deformation or of rupture, is dependent upon the hardness of the rock, and per unit of surface is a constant for each kind of rock under conditions of maximum efficiency.

It is necessary to see, at the beginning of the consideration, that the total of all the new surface of all pieces contained in a definite quantity of crushed rock of given hardness represents the accomplishment of crushing, whatever energy was required to do the work. The mass is conceived as being broken out from a solid mass of rock, and broken down to the condition in which we have it. Such rating may be made conveniently by employing Gates' reciprocal. In any case, we must see that the work is

proportioned to the surface, and is not dependent upon a third linear unit that is distributed indefinitely within the volume of the uncrushed pieces.

Mr. H. Stadler,² under the opinion that he had discovered important contradictions to prevailing beliefs, introduced a third dimension, representing the dimension of the pieces. The third dimension would make the work accomplished in crushing each particle dependent, not upon the surface, but upon the volume, and correspondingly would alter the basis of representation of the work expended upon a given mass or accumulation of these pieces. The idea arose from the fact that there is a force normal to the unbroken surface, functioning as deformation, against which all rupture must be performed, through a distance influenced by the diameter of the particle. Modifying the surface by the new factor changes surface into solid, raises the equation to the third degree, and suggests volumetric expression of accomplishment for the total of the solid particles.

We must see, however, that many factors could be introduced that would add to the conception of the occurrences of crushing and seem to depart from surface representation. But like this one, they are not constant and are not a necessary part. Even if the effects coincided to a large extent with this supposed dimension, they would only the more deeply involve us in a misconception and the more effectually conceal the need of a true interpretation to show the nature of the work. Mr. Stadler fails to bring out the time factor that conditions the depth of plastic deformation, and fails to observe the real difference between the elastic and the plastic factors. He would have to tell us that, by his reasoning, the work done in sawing a plank into two shorter planks is conditioned not upon the cross-section, made by the given saw, but depends upon the length of the plank. Similarly, by such reasoning, knowing of the existence of elastic strain, and knowing that it is present not only within the rock but beneath all acting surfaces, he would have to rate as useful, the work done upon the metal liners, conditioned not by the size of the ore, but by the size of the machine. He refers to the work of Friedrich Kick as confirming his own conclusions in a statement that he singles out as "Kick's Law," drawing conclu-

² *Ibid.*

sions, which we are compelled to observe that practice does not support.

The component that deformation actually introduces is a vague quantity that varies, sometimes, somewhat according to the dimension, but is dependent upon the manner in which the operation is performed. The deformation that is elastic, is available, and may be given back again in doing work; and, in efficient operation, should be recoverable in appreciable proportion. The deformation that is plastic is permanent deformation. It is accomplished with internal friction. The energy that produces it practically takes the form of heat. It is variable, depending upon many conditions, such as prevailing temperature and velocity; but so far as it occurs, it should be measurable as heat. No person can desire to include this waste heat as a component of the useful work of crushing. Everyone can see that it is possible to produce much heat with no appreciable crushing. For example, one may hammer a small mass of malleable lead until it is hot without the beginning of a rupture. Similarly, it is possible to do much crushing with little heat, increasing velocity and shortening the time until deformation becomes much diminished. The heat should attract our attention as one of the losses, along with vibration or with the noise that is made. It doubtless should be measured, but to put heat and deformation into the accomplishment of crushing would pervert all ideas of efficiency, and hopelessly conceal real differences under a changeable and false standard.

It is, in a measure, objectionable, and may be found to be unfair, to compare the results obtained in coarse crushing with other results, perhaps corresponding, obtained in fine crushing. Hard grains, which escape fracture in the coarse crushing, consume great power in fine grinding. Cleavage, jointing, and minute fissuring, introduce lines of weakness that often develop at some definite size. In all these cases we are dealing with a rock having qualified hardness. The qualification of hardness, solely as to direction, becomes eliminated in the average hardness of the rock in all directions. The hardness qualified as to size, through nodulization, crystallization or other prevailing structural peculiarities, are qualities which crushing-tests, in many cases, are designed to show. None of these qualifications impose permanent complications upon interpretation. Computations are

based upon homogeneous rock. Departure from homogeneity is recognized and given such weight as the determined conditions may show to be required. It is imperative that the basis of accomplishment be unequivocal here for the true estimate of these highly important, comparative effects.

Crushed material, qualified as to the shape of the crushed fragments, imposes a wider approximation and demands empirical estimation in terms of screen sizes. The reduction coefficient, in terms of energy, is independent of the shape, so long as similarity of shape may be everywhere assumed. The averaging of dissimilar shapes, and the expression of size in terms of the screen opening, or of the observed average dimension of the pieces, is not a rough measurement, relative to the approximations that are required elsewhere in screening or classification. The calculation and consideration of size, at present, requires the assumption of some average or ideal shape. This may be the sphere, the cube, the tetrahedron, or some other definite and recognized solid form. The cube often is chosen for its simplicity but the average surface, as well as the average volume, relative to the average diameter or to the screen dimension, is a factor yet to be determined for average materials.

The work done upon the different sizes is held, therefore, as a relation rather than a dimension; the surface of a cube being assumed to give a basis of measurement upon which this proportionality may be conceived. Brunton measured the relation between the volume of the particle and the dimension of the screen opening years ago,³ but his conclusions were harmed by the imperfectness of the screens that were then available. Departure from the shape of the cube may be cared for by the use of an equalizing factor, when known, but the study of crushing has not advanced to a point that justifies attention first to this. Qualifications as to shape are not, relatively, an obstacle to the determination of accomplishment in units. The one predominating relation is derived from the estimated total of surface within the given mass. With constants as to shape and others as to hardness, and others specific to the size, we can pronounce upon efficiency in operation, by the measurement of the size, giving the expression of the total surface. Without knowing the size, and

³ "The Theory and Practice of Ore Sampling," *T. A. I. M. E.*, 1895, 25, p. 835 *et seq.*

seeing that the surface is the accomplishment, we cannot go far into the useful work that requires to be done.

When, with patience, we can separate the crushed products into graded lots, and make close estimates upon the quantity of these lots, and, as accurately, determine the size, we may place some arbitrary value in energy units upon accomplishment, or surface, for given materials, crushed under known conditions. By the definition of crushing itself, the work is the production of new ruptures. The accomplishment is the extent of such ruptures shown by the surface produced. It should be clear that the part of deformation which takes the form of elastic stress is recoverable for doing work in many ways that do not require explanation here. It should be clear that the part of deformation which is plastic diminishes in extent with increasing velocity of the movement which produces the rupture, as well as with the proper direction and application of the forces. Under the influences of these compensating and power-reducing conditions the loss by deformation should approach zero, under ideal conditions, and the attainment of maximum efficiency should imply the securing of this end. As this maximum efficiency is approached, all loss diminishes inclusive of the loss by deformation. The energy expended then becomes confined to the molecules that lie contiguous to the plane of fracture. These are represented by the area of the fracture.

Much relative to efficiency we are able now to state. With hard rock the work-value is high. With tough rock the work depends greatly upon the manner of application. With a slow application of forces there is a heavy loss by plastic deformation. With fine crushing it is difficult to prevent the heavy loss by surface friction. With fissile or cleavable rock only one out of three or more necessary cuts is made easy by the qualified hardness. We can crush in such a manner as to bring out the highest resistance of deformation, developing static forces functioned into volume, or we can diminish these to a large extent. We can do any of the work of crushing in a laborious way, or in an efficient way; but the work accomplished remains the same, and is measured by the surface which is made. It would be highly desirable if we could agree upon this statement now or definitely oppose it and find reason in our belief. The development of our units of accomplishment, the growth of methods of representing the results

of practice, and the whole understanding of efficiency await this judgment.

It appears necessary to make this statement in order that none among us fall into a state of patient skepticism, awaiting a kind of demonstration that is not to be expected. From the considerations into which we have entered, it should be clear that misconception has been due to a failure to analyze the qualities of deformation. In much of the work that engineering has to do, and in the case of all the inductions of scientific theory, the reasoned fact covers the shortcomings of material demonstration, and offers the only standard of judgment that is fundamental in last analysis. It is not now so much the proof of experiment that we require as definition of what we understand that crushing means. This will give us the basis for interpreting efficiency in the work we do, and permit milling practice to pass on to the attention of more important problems.

THE Department of Terrestrial Magnetism of the Carnegie Institution has made a new analysis of the magnetic field of the earth. Of the magnetic forces manifest on the surface of the earth, 93 per cent. are due to electrical or magnetic forces within the earth, 3 per cent. to electrical systems in the atmosphere, while "the remaining portion, about 4 per cent., is apparently to be ascribed either to vertical earth currents which pass through the atmosphere into the earth and out again, or to an affect similar to the deviation of the compass needle caused by forces set in operation during the earth's rotation, or to both causes combined. . . . The earth's magnetic moment is diminishing; the annual rate of decrease during the past sixty years has been one part in 1200." G. F. S.

Effect of Pressure upon Optical Absorption. MISS F. G. WICK. (*Phys. Rev.*, March, 1923.)—These experiments carried out in the laboratory of P. W. Bridgman, showed that small effects do exist. The results are chiefly qualitative. Light from a carbon arc was transmitted through solutions and solids at normal pressure and at pressures up to 1500 atmospheres and the spectra were photographed. Generally the effect of increasing pressure was similar to that due to a lowering of temperature. In solutions increase of pressure has, in general, an effect like that caused by diluting the solution. Sometimes bands are shifted either toward the red or toward the violet or become more prominent at high pressures.

G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

A METHOD FOR THE MEASUREMENT OF SOUND INTENSITY.¹

By J. C. Karcher.

[ABSTRACT.]

A METHOD for the measurement of sound intensity is presented which has a wide range of sensitivity, permits sound approaching the threshold value of audibility to be measured and does not necessitate the calibration of an amplifier.

The measuring instrument consists of a magneto-phone or electrostatic transmitter, and two coils whose mutual inductance can be varied by known amounts.

The e.m.f. generated by the magneto-phone due to its presence in the sound field is compared with the e.m.f. generated in one coil when the other carries a known current. The comparisons are made by successively impressing the e.m.f.'s upon an indicating instrument consisting of an amplifier, a rectifier, and galvanometer. The mutual inductance between the two coils is varied until the two e.m.f.'s are equal. The e.m.f. generated in the second coil can be computed, and since the sound intensity at the magneto-phone is proportional to the square of the e.m.f. generated, a means of making sound intensity measurements is presented.

Absolute calibration is made by comparison with a Rayleigh disc.

AERONAUTIC INSTRUMENTS.²

By Franklin L. Hunt.

[ABSTRACT.]

THIS paper describes various aeronautic instruments and will be useful to those interested in the general aspects of the aeronautic instrument art.³ The instruments considered are as follows:

* Communicated by the Director.

¹ Scientific Paper, No. 473, price five cents.

² Technologic Paper No. 237, price twenty cents.

³ For a more detailed discussion see Reports Nos. 125-132, inclusive, National Advisory Committee for Aeronautics, 1922.

ALTITUDE INSTRUMENTS—ALTIMETERS, BAROGRAPHS, STATOSCOPES.

Altimeters and barographs are used to indicate altitude. They are the same in principle as aneroid barometers. Changes in altitude are indicated by the expansion or contraction of one or more evacuated metal capsules which are maintained distended by springs.

Statoscopes are used in lighter-than-air craft to show small changes in altitude. Air in a heat-insulated container expands or contracts with changes of external atmospheric pressure, thereby causing liquid in a glass trap attached to the container to move and thus indicate rise or fall.

SPEED INSTRUMENTS—AIR-SPEED INDICATORS, GROUND-SPEED INDICATORS, RATE-OF-CLIMB INDICATORS.

Air-speed indicators show the speed of aircraft relative to the air. Ground-speed indicators give the speed with reference to the ground. The former depend for their action on the pressure developed in Pitot or Venturi nozzles or on pressure plates, by the motion of the airplane; or on the speed of rotation of cup anemometers or small air propellers. The nozzle pressure is measured by a sensitive pressure gage.

Ground-speed indicators depend on measuring with a stop watch the time for an object on the ground to pass between two sighting points on the ground-speed indicator or upon some rotating or reciprocating optical device which neutralizes the apparent motion of objects on the ground as seen through a telescope. Devices in which the time integral of the accelerations of the airplane are found mechanically have been proposed, but these are unsuccessful. Directional wireless telegraphy triangulation methods are also used.

Rate-of-climb indicators are like statoscopes except that the air container is connected to the external air through a fine capillary tube instead of a trap. One side of the container is a flexible diaphragm which expands and contracts under the pressure lag caused by the capillary tube, thus indicating rate of ascent and descent. Liquid manometers are also sometimes used to measure the difference in pressure between the container and the external air.

ORIENTATION INSTRUMENTS—COMPASSES, TURN
INDICATORS, INCLINOMETERS.

Aircraft compasses are the same in principle as marine compasses but are much lighter in construction. They are ordinarily of quick period. To avoid the disturbing effect of masses of iron in the airplane motor distant reading compasses have been tried. One method is to use the earth's magnetic field to develop a current in a rotating coil of wire. Another uses the resistance changes of selenium cells exposed by the motion of the compass card to the light from incandescent lamps.

Turn indicators are essentially gyroscopic rotors which tend to maintain their direction in space when the airplane deviates. Rotors driven by the impact of an air stream on the serrated edge of the rotor and also those in which the rotor is the armature of an electric motor are used.

Inclinometers are either liquid bubble levels or gyroscopic rotors. The former indicate the inclination of aircraft with reference to the resultant of gravity and centrifugal force and the latter with reference to the true vertical.

ENGINE INSTRUMENTS—TACHOMETERS, PRESSURE GAGES, GASOLINE
GAGES, GASOLINE FLOW INDICATORS, THERMOMETERS.

Tachometers indicate the rate of revolution of the aircraft propeller. The two types most commonly used are the centrifugal, which is the same in principle as the familiar ball governor, and the chronometric, in which the speed is measured by the amount of motion of a toothed rack or gear system in a measured interval of time determined by a clockwork escapement. Other types include magnetic tachometers in which a permanent magnet is rotated near a conducting disc, thereby dragging the disc by virtue of the eddy currents produced; electromagnetic tachometers depending on the current developed by a magneto which is connected to an indicating galvanometer; air drag or viscosity tachometer in which one disc or cylinder attached to the engine shaft rotates another disc by virtue of the viscosity of the air film between them; air pump type, consisting essentially of an air pump which forces air through a pressure indicator.

Air and oil pressure gages used to indicate the air pressure in the gasoline tank and the oil pressure of the engine lubricating system are ordinarily of the familiar Bourdon tube type.

Gasoline gages are used to measure the gasoline supply. The most common type consists of a float which rests on the surface of the gasoline and is connected to the indicating mechanism by a metal rod or flexible cord. Another type depends upon the hydrostatic pressure of the gasoline in the tank.

Gasoline flow indicators show the rate of consumption of gasoline. In one type a metal vane restrained by a coiled spring is deflected by the gasoline as it flows through the instrument. In another, gasoline is forced out through a slit in a vertical metal tube surrounded by a concentric glass tube. The height reached by the gasoline in the metal tube as it flows through the slit depends on the rate of consumption and is indicated by a small rider which moves up and down in the slit.

Thermometers are used to indicate the temperature of the radiator water and oil supply of the engine. They are either of vapor pressure or liquid filled type according as they depend upon the variation of pressure of the vapor of a volatile liquid or the expansion of a liquid with change of temperature. A bulb containing the liquid located at the point whose temperature is to be taken is connected by small metal tubing to an indicator which is ordinarily a Bourdon tube gage.

**NAVIGATING INSTRUMENTS—MAPS, DEAD RECKONING INSTRUMENTS,
ASTRONOMICAL INSTRUMENTS, RADIO DIRECTION FINDER.**

Maps and charts are carried on long distance cross-country flights. The position of the aircraft can also be calculated from readings of the compass, air speed, ground speed and drift with reference to the ground. Where the earth is not visible astronomical methods involving the use of sextants are available. The use of radio direction finders in conjunction with radio sending stations is also being used.

**SPECIAL INSTRUMENTS AND ACCESSORIES—OXYGEN INSTRUMENTS, RE-
CORDING INSTRUMENTS, STRUT AND GAS TEMPERATURE THERMOME-
TERS, TIME PIECES, MANOMETERS, HYDROGEN LEAK DETECTORS.**

Oxygen instruments supply artificial oxygen to aviators at high altitudes. The gas is either compressed into cylinders or carried in liquid form and delivered to the aviator through pressure regulators which automatically control the supply in accordance with the altitude.

Recording instruments are for experimental work and airplane performance tests where permanent records of altitude, air speed, rate of revolution of the engine, rate of ascent and descent, temperature and humidity are required. These instruments are the same in principle as the indicating instrument of the corresponding type previously described but are provided with recording attachments.

Strut thermometers are used on airplanes to determine the temperature of the surrounding air and gas thermometers on lighter-than-air craft to indicate the temperature of the gas in the bags. Strut thermometers are usually ordinary liquid thermometers. They may also be of the liquid filled or vapor-pressure type described above. Electric resistance thermometers are frequently used to indicate gas temperature.

A clock or watch is carried in most aircraft. Any clock which will stand the shocks of landing and vibration may be used.

Lighter-than-air craft are equipped with manometers to control the pressure of the gas in the bags. Hydrogen leak detectors are used to indicate when gas is escaping from the bags of lighter-than-air craft. One type depends upon the pressure developed in an inclosed chamber provided with a semi-permeable porcelain back by the escaping hydrogen diffusing into the chamber. The pressure is measured by the motion of a flexible metal diaphragm.

The original paper is illustrated by many photographs of the most recent types of aircraft instruments.

ARLINGTON BUILDING.⁴

By Louis J. Larson and Serge N. Petrenko.

[ABSTRACT.]

THE hollow tile and reinforced concrete floors of the Arlington Building, Washington, D. C., were loaded and the deformations measured. This was, at the time, the first test upon this type of construction in which strain-gage measurements were taken.

The floor slab was formed by rows of hollow tiles spaced four inches in each direction. The reinforcing steel was placed in

⁴ Technologic Paper No. 236, price fifteen cents.

these spaces and concrete poured around it and into the open ends of the tiles.

The columns are steel H-sections surrounded by a thick casing of concrete. The beams and girders have steel I-beams encased in concrete. These beams are generally near the bottom and may be considered the tension reinforcement.

The building, intended for a hotel, was originally designed for a live load of 75 lb./ft.² On account of the purchase by the government for an office building the live load was increased to 100 lb./ft.² and to care for this additional load, a 2-inch layer of concrete was placed on top of the tiles. This type of construction was new in many respects and the design was considerably lighter than that recommended by the "Joint Committee on Concrete and Reinforced Concrete." For these reasons, it was desired to find the live load which could be placed on the floor panels before too high stresses were developed. It was desired, also, to secure as much information as possible on the action of the hollow tile slab.

The panels, having various ratios of length to width (from 1.05 to 1.86) were loaded with sand bags, separated by aisles to prevent arching, some up to 380 lb./ft.² The loading schedule was intended to produce maximum positive and maximum negative moments and to enable the study of the effect of transferring load to an adjacent panel.

The deformation readings consisted of strain-gage measurements on the steel and concrete and deflection measurements on the slabs and on the beams. The gage lines were located at positions of maximum positive and maximum negative moment and in some panels in other places to study the distribution of bending moments throughout the panel. The deflection readings were taken at the centre of each panel and at the middle of the supporting beams. The corrections made necessary by the considerable fluctuations of temperature were based on readings on standard bars.

The maximum stresses developed in the slab were about 27,500 lb./in.² in the negative reinforcement and 24,000 lb./in.² in the positive reinforcement. Both stresses were developed at the load of 335 lb./ft.² The stresses developed in the reinforcing

I-beams of the girders were lower. The maximum recorded compressive stress in the concrete was about 1600 lb./in.²

The distribution of the cracks in the concrete furnished an indication of the distribution of the stresses at an early stage of the test. The first cracks observed were diagonal ones on the bottom of the slab. They occurred at about the same time as the cracks on the top which extended across the corners and at right angles to those on the bottom. The cracking of the concrete was accompanied by a considerable increase of the stresses in the reinforcing steel. The study of the cracks and the stresses shows that in a test of this kind, the deformations, though measured at positions of maximum moment, will fall far short of showing the maximum stresses unless the gage lines are located across, or very close to, the principal cracks. Thus, in some cases, the stresses observed at positions of maximum moment and at the gage lines crossed by cracks were 16,000 and 23,000 lb./in.², while stresses in gage lines 12 inches from the cracks were 4000 and 5000 lb./in.², respectively.

The effect of time under load was very pronounced in the first twenty hours and comparatively small later.

The effect of increasing the ratio of the length to the width of the panel was to increase the moments carried by the positive and the negative reinforcement in the short span and a corresponding decrease of the moments in the long span.

The beams offered very little resistance to torsion and the stresses in the negative reinforcement across the beam were little affected by the transfer of load across the beam.

The increase of the deformation in the reinforcement due to long-continued loading was greater than that in the concrete. This probably was partly due to the assistance of the clay tiles in resisting the compressive deformation because of the clay tiles yielding less than the concrete.

The moment coefficients are generally small due to the low stresses and are not proposed for use in design but to show the relative amount of bending moment carried in the two directions.

From the comparison of these results with those obtained from tests of simple beams, it appears that the factor of safety of the construction is apparently higher than 2.

METHODS OF MEASUREMENT OF PROPERTIES OF ELECTRICAL INSULATING MATERIALS.⁵

By J. H. Dellinger and J. L. Preston.

[ABSTRACT.]

THE Bureau of Standards receives frequent requests for information on the methods which it has found practicable for making measurements of properties of electrical insulating materials. The methods are described in this paper, and are the methods that were used in the research described in the previous publication by the same authors, Technologic Paper No. 216, "Properties of Electrical Insulating Materials of the Laminated, Phenol-methylene Type." The reasons for selecting certain physical properties for measurement in a research on electrical insulating materials, and the definitions of the properties are detailed in that paper. The same considerations apply in the measurement of many types of insulating materials besides the laminated phenolic materials. The properties for which methods of measurement are described are: Phase difference and dielectric constant at radio frequencies, voltage effects at radio frequencies, volume resistivity, surface resistivity, density, moisture absorption, tensile strength, transverse strength, hardness, impact strength, permanent distortion, machining qualities, thermal expansivity, and effects of chemicals.

Insulating materials are not perfect in their insulating qualities, and there is a certain amount of power absorption in them when used in a circuit in which alternating current flows. This effect is particularly important when the frequency is high, and it has been shown in fact that the power loss is the best single property that gives an indication of the suitability of an insulating material for use in high-frequency (radio) apparatus. The power loss can be expressed by a number of constants: The resistance, phase difference, phase angle, power factor, sharpness of resonance, and decrement. The simplest of these expressions for the power loss is the phase difference. It and related quantities are obtained by measurement of the frequency of the alternating current used and the resistance and capacity of a condenser made of the material to be tested. The measurement of the radio-frequency resistance is the most difficult part of this procedure.

⁵ Scientific Paper No. 471, price fifteen cents.

Complete details of this and the other measuring methods are given in the paper. The dielectric constant is obtained as a result of the phase difference measuring procedure, supplemented by measurements of area and thickness of the sample.

The measurement of voltage effects is described for radio frequencies only, as injurious effects are caused at much lower voltages for radio frequencies than for lower frequencies. A small sample of the material is mounted in parallel with a condenser and observation is made of the voltage required to arc over a 2-cm. surface separation between metal electrodes.

Electricity leaks above the surface of an insulator as well as through its volume, and so it is necessary to determine both volume resistivity and surface resistivity. They are obtained from measurements of direct-current resistance and dimensions of sample. Atmospheric humidity affects the surface resistivity, and must be carefully controlled and measured.

Density and moisture absorption are measured by weight in air and in water. The moisture absorption is for a period of twenty-four hours.

Tensile strength is measured on a standard testing machine, using special adapters in the jaws to render the alignment of the test sample free and automatic. Modulus of elasticity (tensile) is measured by the aid of an extensometer between gage marks two inches apart.

Modulus of rupture and modulus of elasticity (transverse) are determined on a sample loaded at centre of a 10-inch span.

The Brinell and Shore scleroscope methods are used for measuring hardness.

Impact strength is obtained from the angular swing of a pendulum hammer which breaks a short slotted sample held in a vise.

Permanent distortion is measured as the permanent sag due to dead loads at the centre of a 12-inch span.

Machining qualities are not susceptible to as exact measurement as other properties. They are practical tests, based on averages obtained by two or more mechanics following a prescribed routine to give the ease of machining, surface finish of machined samples, effect on machine tools for specimens sawed, turned, machine and die threaded, tapped, drilled, and shaped.

Thermal expansivity is measured on a specimen 30 cm. long either in oil or air. Microscopes are used to measure length changes and thermocouples to measure temperature.

The chemical effects include the effects of sulphuric acid and caustic soda. The sample is immersed for a period from two to sixty days, and the weight and hardness determined at specified intervals.

The information obtained by making this series of measurements on a given material is quite comprehensive, and should make possible the selection of the best material for a given use.

SERIES IN THE ARC SPECTRUM OF MOLYBDENUM.^o

By C. C. Kiess.

[ABSTRACT.]

MANY of the strong lines of the arc spectrum of Mo have been found to be members of series. These are of several types. Narrow triplets characterized by the frequency differences 121.5 and 87.0 have been arranged into the series $1S - mP_1$, $2P_1 - mS$ and $2P_1 - mD$. Widely separated triplets, between which the frequency differences 448.5 and 257.5 exist, form the series $1s - mp_1$, $2p_1 - ms$ and $2p_1 - md_1$. Parallel to these wide triplet series are other series $1s - (mp_1 + k_1)$, $(2p_1 - k_1) - ms$ and $(2p_1 - k_1) - md_1$, of which the separations 379.9 and 233.4 are characteristic. The limits of these series have been calculated with formulas of the Ritz type and with the aid of the inter-series combination-lines $1s - 2P_2$, $1s - 2P_3$, $1S - 2p_2$, and $1S - 2p_3$. From the known values of $1s$ and $2p_1$ it follows that the resonance and ionization potentials of Mo are 3.25 volts and 7.35 volts, respectively. In addition to the triplets there occur in the spectrum of Mo, groups of 9, 10, and 13 lines known as multiplets, which arise from the combinations of the various threefold and fivefold levels which exist beyond the $1s$ level of the atom.

WOOL is produced in every State in the Union, according to reports of the United States Department of Agriculture. In 1922 production totalled 219,095,000 pounds (not including pulled wool) compared with 225,546,000 pounds in 1921. Wyoming and Texas led in production in 1922, having produced 22,500,000 pounds and 19,300,000 pounds, respectively.

^o Scientific Paper No. 474.

NOTES FROM THE RESEARCH LABORATORY,
EASTMAN KODAK COMPANY.*

A SPECIAL SENSITOMETER FOR THE STUDY OF THE
PHOTOGRAPHIC RECIPROCITY LAW.¹

By L. A. Jones.

A SENSITOMETER built especially for a critical study of the failure of the reciprocity law is described. The requirements of such a sensitometer are outlined and a detailed description of how these various requirements are met is given. Exposures are given by means of a rotating sector wheel which is driven by a constant speed motor. The arrangement is such that a plate is exposed by a single turn of the sector wheel, thus eliminating the intermittency effect inherent in the usual type of sector wheel sensitometer. By means of a series of gears, it is possible to vary the angular rotational velocity of the sector wheel over a very wide range so that exposures automatically timed may be given, varying from .0002 second up to 16 hours. The required variation in the illumination incident on the photographic plate during exposure is obtained in part by the variation of the distance between the light source and the plate and in part by a variation in the effective size of source. An intensity range of about one to one million is available. The sector wheel is driven by a constant speed governed motor which can be checked directly against the beat of a seconds pendulum.

As a result of experimental work conducted near Block Island by the Subaqueous Ranging Section of the Coast Artillery Corps, it has been established that the speed of sound in salt water increases 2.8 metres per second for each Centigrade degree of increase in temperature from 0° to 20° C. The effects of change of density and salinity are included in the increase stated. They are small in comparison with the temperature effect. (*Phys. Rev.*, March, 1923.)
G. F. S.

* Communicated by the Director.

¹ Communication No. 161 from the Research Laboratory of the Eastman Kodak Company and published in *Jour. Opt. Soc. and Amer. Rev. Sci. Inst.*, April, 1923, p. 305.

Increasing Rubber Output.—Oil and rubber are two of the most important world staples at the present time and struggles to obtain control of regions in which they may be obtained are disturbing the diplomatic relations of the great nations. A wonderful increase of rubber supply has resulted from the cultivated plants, just as the supply of quinine has been increased by the cultivation of the cinchona trees. Apart from the advantage of extending the area in which a given plant grows is the improvement of the strain so as to secure a greater yield or to develop individuals less subject to damage from weather conditions or enemies. The growth of the plantation rubber industry is shown by figures given in Tuttle's recent book on the "Analysis of Rubber." In 1903, 25 tons was the output of plantation rubber, but in 1919, 360,000 tons were produced. Many plants carry milky juices, technically called "latex," but only a few so far known are of commercial value. *Hevea brasiliensis* Muell. Arg., is the most important source. The issue of the *India Rubber World* for May, 1923, gives an interesting and detailed account of methods of bud-grafting for improving the yield of latex. Investigations in some plantations showed that a considerable proportion of trees yielded but little of the desired material, while other trees were fruitful. At present the average production is about 5 pounds per tree per year, but instances of as much as ten times this yield have been observed. From analogy of other plants it would seem that the grafting of buds of the high-yielding trees upon one year seedlings would insure the development of a high-grade stock, and some experiments lately undertaken in the Dutch East Indies have been sufficiently encouraging to warrant more extended work.

In the issue of the *India Rubber World* from which the above note is taken, the article is by G. E. Perry, presenting the histology of the *H. brasiliensis*, liberally illustrated. Mr. Perry, who is a graduate of the Massachusetts Agricultural College, spent several years in the rubber-producing regions. At present only a small area of bud-grafted plants is under cultivation. H. L.

Magnetic Measurements in Normandy. C. E. BRAZIER. (*Comptes Rendus*, April 3, 1923.)—All the observations were made in the two departments separated by the lower reaches of the Seine. Since 1896 the mean declination has changed by 3° and the inclination by $.29^\circ$. Both these changes are diminutions, while the intensity has increased by .0014 dyne. It appears, however, that the secular variation is not uniform even over so restricted a region. Four stations on the coast, including Di  ppe and Fecamp, show values distinctly less than the average, 2.57° , $.25^\circ$, and .0006 dyne. "This fact, which seems not to proceed from errors of observation, suggests the idea that the displacement of isomagnetic lines must be accompanied by changes in their form quite small, yet appreciable at the end of a score of years." G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

FURFURAL FROM CORNCOBS.¹

I—FACTORS INFLUENCING THE FURFURAL YIELD IN THE STEAM-DIGESTION PROCESS.

By F. B. LaForge.

[ABSTRACT.]

THE reactions involved in the production of furfural from corncobs by the steam-digestion process occur in three stages. The conversion of the pentosans into furfural does not take place quantitatively; the yield depends upon the temperature, the time, and the ratio of the amount of cobs to the amount of water employed. The optimum conditions of operation were determined in order to apply them to larger-scale investigations. These conditions are a temperature of about 180° C., a reaction period of about two hours, and a ratio of cobs to water of not greater than 1 : 4.

CATALYTIC OXIDATION OF ANTHRACENE TO ANTHRAQUINONE.²

By C. E. Senseman and O. A. Nelson.

[ABSTRACT.]

A CATALYTIC method for the preparation of anthraquinone, an important intermediate in the manufacture of dyes, has been patented by Gibbs and Conover, and worked out in the Bureau of Chemistry.

The apparatus consists essentially of a carburettor, a reaction chamber, and a sublimator, all made of glass and heated by well-insulated electric heaters. The carburettor is built with two air inlets—one arranged so that the air will sweep over the molten anthracene, thus carrying a definite quantity of the hydrocarbon into the reaction chamber, the other arranged so as not to interfere with the work of the first, but to vary the air-anthracene concentration as desired.

The catalyst, vanadium pentoxide, may be supported (1) by

* Communicated by the Chief of the Bureau.

¹ Published in *J. Ind. Eng. Chem.*, 15 (May, 1923) : 499.

² Published in *J. Ind. Eng. Chem.*, 15 (May, 1923) : 521.

boats, (2) by discs, (3) by pumice, or (4) by fusing to a glass tube.

The sublimers, as used during most of the runs, consists of a Kjeldahl flask with neck removed, jointed to the reaction chamber by a ground-glass joint.

The maximum yield obtained was 81.2 per cent. of the theoretical.

On a New Method for the Generation of Sound-waves. JUL. HARTMANN, Copenhagen. (*Phys. Rev.*, Dec., 1922.)—"If air is allowed to stream from a container in which the absolute pressure is more than 1.9 atm.—that is, the over-pressure is higher than 0.9 atm.—through a hole or a short bore out into the free atmosphere, a jet is produced which exhibits a peculiar periodic structure. . . . It is now known that the periodical structure is closely connected with the fact of the velocity of the jet, with sufficiently high over-pressure, being higher than that of the sound." A study of the jet made with a Pitot pressure gauge shows that the pressure rises and falls as we move outward along the stream of air. There are thus portions of the jet where the pressure increases at the same time with the distance from the orifice. If the fine aperture of a bulb containing air be introduced into one of these intervals of instability, air will alternately flow into and out of the bulb and a tone is produced. Such air waves are, however, of less value than those obtained by inserting the mouth of a plain cylindrical resonator into an interval of instability. The wave thus produced has a length equal to about four times the length of the resonator. "It (the intensity) is ordinarily very high, due undoubtedly partly to the high density of the energy in the air-jet, partly to a comparatively very high efficiency of the generator. (Provisory measurements seem to prove that the efficiency at about 20,000 periods per sec. is as high as 10 per cent.) As to the frequency, resonance-oscillations, *i.e.*, pure acoustic oscillations of 100,000 periods or more, can easily be produced by means of a jet of atmospheric air. With a jet of hydrogen a frequency of more than 300,000 can be obtained. As a matter of fact the author has been able to produce intense sound-waves of 340,000 periods, and in all probability there will be nothing to prevent the production of still higher frequencies. The author therefore holds the opinion that the air-jet in connection with a resonator furnishes a means for producing intensive, pure acoustic oscillations of higher frequencies than has hitherto been possible." The structure of the apparatus is shown and it is not complicated.

"With a resonator of about 10,000 periods per sec. the produced tone was with even rather small over-pressures almost unbearably intensive and left the observer with a physiological after-effect of several hours' duration."

G. F. S.

NOTES FROM THE U. S. BUREAU OF MINES.*

THE METALLURGICAL TREATMENT OF ZINC RETORT RESIDUES.

By B. M. O'Hara.

THE residues resulting from the retort distillation of zinc ores have from 40 to 75 per cent. of the weight of the original ore and contain from 5 to 15 per cent. zinc. A rough estimate indicates that approximately 450,000 tons of residue are produced annually in the United States, containing about 36,000 tons of zinc. Besides the current production of residues there are at many smelter sites large accumulations from past operations which are available for treatment if this can be done profitably. In addition to their zinc content the residues contain much unconsumed coal, which has been carbonized during the distillation process, and those from most western ores also contain lead and silver.

A survey was recently made by the Bureau of Mines, in coöperation with the Missouri School of Mines and Metallurgy, of processes which are in use or which have been suggested for the treatment of retort residues.

These methods may be classified as follows:

- (1) Smelting directly in the lead blast furnace for the recovery of lead, copper, and precious metals.
 - a. Residues mixed in small proportions with ore charge.
 - b. Residues smelted alone with the necessary fluxes.
- (2) Burning and sintering to remove carbon and furnish a desirable product for the lead blast furnace, followed by blast furnace smelting.
- (3) Dry screening.
 - a. For the recovery of coke.
 - b. For the concentration of lead and precious metals into an enriched product.
- (4) Magnetic separation.
- (5) Wet concentration.
 - a. For the recovery of lead and precious metals only.
 - b. For the recovery of zinc and coke.

* Communicated by H. Foster Bain, Director, Bureau of Mines.

(6) Burning on Wetherill grates for the production of zinc oxide.

(7) Miscellaneous.

Most of these methods are, or have been, in actual use in one or more zinc smelters. Different methods are suited to different conditions; some have been successful in certain plants and unsuccessful in others.

It is probable that conditions are such at some plants that the retort residues cannot be profitably treated by any method; on the other hand, it is probable that many companies which do not now treat their residues could do so, if the proper method were chosen, and properly adapted to the particular conditions existing.

The treatment of old condensers is simpler than that of retort residues, and it seems that most zinc smelters could with profit build at least a simple jigging plant for their concentration. Further details will be found in Serial 2475, which was read at the meeting of the American Zinc Institute, May 7 and 8, 1923.

FLUORSPAR MINING IN THE WESTERN STATES.

By Raymond B. Ladoo.

IN order to obtain comprehensive and authentic information on fluorspar mining in the western states, the writer, together with and at the request of representatives of some of the largest fluorspar producers of the Illinois-Kentucky district, spent the month of April, 1922, in examining all western fluorspar deposits (of which record was available) believed to be of possible commercial importance.

After weighing all evidence by actual examinations and by available information from other sources, the following conclusions were reached:

(1) With one exception, all of the deposits worked have been so small, or so far from transportation, or contain fluorspar so mixed with silica or barite or both, that profitable production of *gravel grade* of fluorspar, acceptable to eastern steel mills under present standards, has been impossible, and the future seems no more promising. There are two small mines which would yield a few hundred tons annually by screening hand-picked ore, but from present indications, these properties do not justify the erection of mills.

(2) With only one exception, the most accessible ore from the mines which have been worked has been removed. The mines are, for the most part, in poor physical condition, and future operations will be increasingly difficult and expensive.

(3) Most of the western mines have long and expensive hauls to railroad, and the ore bodies are too small to justify the cost of installing improved methods of transportation, or modern mining and milling equipment.

(4) The production of *acid fluorspar* west of the Mississippi River from ore bodies now known probably will not exceed 100 tons annually. It is believed that not over 3000 tons of *ground fluorspar* can be annually produced, of which one-third will be low grade.

It was estimated that the properties visited in the western states can produce for a few years a maximum of 13,000 tons annually of a grade of *gravel* analyzing on an average 5 per cent. or higher in barite, and a maximum of 4000 tons of *fluxing lump*. The western steel mills, on account of the difficulty of obtaining fluorspar in gravel form, have been accustomed to use in their open-hearth furnaces both lump and gravel. The estimated consumption of the western mills is 10,000 tons annually, and they will probably continue to utilize western fluorspar on account of the high freight rates applicable to the Illinois-Kentucky product.

The foregoing estimates of production represent the theoretical possibilities of the western mines, which it is not believed will be reached in practice. Further details will be found in Serial 2480, recently issued by the bureau.

LUBRICATING OILS FROM PACIFIC COAST PETROLEUM.

By Earl C. Lane and N. F. LeJeune.

CALIFORNIA crudes differ in many characteristics from the petroleum produced in other parts of the United States, and the claim has been made that some of the present Federal specifications for petroleum products tend to discriminate against California products. The bureau is making a survey to determine what particular specification requirements California petroleum products characteristically fail to meet, how widely the products deviate from these requirements, and if possible to show whether the fault lies with the specifications or the products, or along what

lines investigation to determine the question should proceed. The properties of gasoline and mineral spirits made from California crudes are described in Serial 2342.

The next group investigated was lubricating oils. Sixty-one samples of lubricating stocks and finished commercial products were generously donated by four of the large refining companies of California. Fifteen samples of automobile lubricating oils, made in California from California crudes, were purchased in the open market. Nine samples of lubricating oils made from gulf coast crude were contributed for comparison by a company in Texas.

Most of the oils meet the specification requirements as regards flash point, viscosity, pour point, corrosion and reaction tests, except for deviations which for the most part are of minor importance.

Of the 78 samples of California oils tested, 90 per cent. failed to meet the requirements of the emulsion and demulsibility tests. It is recognized that emulsion tests have not yet been satisfactorily standardized and possibly in a commercial laboratory some of the samples would have been passed as complying with these requirements. In this work, results of emulsion and demulsibility tests were rigidly interpreted. Also, the organic acidity of many of the samples is above the limit permitted by the specifications. It has been suggested that failure to pass emulsion and acidity requirements may have been caused by contamination with soldering flux from the containers. This hardly seems possible, as the gulf coast samples were much more resistant to emulsification and low in acidity although they were stored in the same kind of cans.

Lubricating oils made from California crudes are being used for many purposes with good satisfaction, and it may be that present requirements as regards organic acidity, emulsion and demulsibility discriminate against them. For certain other oils, however, these tests have been found of advantage, and it seems that the relation between these and other tests and service performance will require careful investigation before the problem can be solved.

Attention is called to the fact that the Federal specifications have been changed since these oils were manufactured and furthermore that the products described in this paper were made for sale in the open market and were not specially prepared to meet

the specifications that were in effect at the time. The close agreement between these oils and the Federal specifications indicates therefore the carefulness and skill in refining possessed by the Pacific Coast refiners.

Detailed tables showing the properties of each sample treated will be found in Serial 2482, recently published.

A New Theory of Vision. FRITZ SCHANZ. (*Zeit. f. Physik.*, Dec. 9, 1922.)—Helmholtz's theory of vision requires three fundamental color sensations and no corresponding nerves have been found. On the other hand, Hering's theory predicates three substances that are modified by the action of light and the presence of these in the eye has not been confirmed. "However long the conflict has lasted, however passionately it has been waged, neither of these theories has been able to establish itself." Leaving these elder theories in their position of stalemate the author frames a new explanation based on the Hallwachs Effect that certain illuminated substances emit electrons. He finds by experiment that solutions of albumin do this.

The light entering the eye is absorbed by the pigment of the retina and electrons are ejected. Their velocity depends on the wave-length of the light to the absorption of which they owe their emission. These electrons, impinging on the rods and cones of the eye, produce an electric current that is led away by the optic nerve. An interesting parallelism, experimentally established between the action in the eye and the Hallwachs Effect, lies in this, that, when monochromatic light falls on the eye, the nerve current that appears is characteristic of the wave-length of the light and that its original strength grows greater the shorter the wave-length is made. Just the same relation between wave-length and the photoelectric current strength has been found by Ladenburg to hold for metals on which light falls.

How can Schanz's theory account for color vision? Let pure spectral monochromatic light fall on the eye. It is absorbed and electrons of a certain velocity are emitted. These are caught on the rods and cones, a current of a strength corresponding to the velocity is developed, and this current is translated into a perception of a color. But the eye cannot distinguish between a sensation due to monochromatic light and one caused by the simultaneous action of two or more lights of properly selected wave-lengths. The explanation of this is not convincing. Suppose two different wave-lengths of light fall on the eye at the same time. Each causes the emission of electrons of a certain velocity. These electrified particles travel side by side and mutually influence the velocity of their neighbors, with the result that they finally all assume the same velocity and produce the same current and ultimately the same sensation of color as if they had all been emitted with the velocity to which they all finally attained.

G. F. S.

West African Palm Oil.—The production of palm oil in West Africa has hitherto been limited almost exclusively to wild trees, and the methods have been inefficient, resulting in a lower yield and a poorer quality than can be obtained by proper means. In recent years a careful study of the subject has been undertaken in the Dutch West Indies, and the development there threatens the British industry, and it will be advisable for British interests to investigate the situation in their own region and also to examine as to whether the palm may not be cultivated in other tropical areas under British control.

The threat of the Dutch competition is along three lines. First, scientific cultivation produces a far greater yield of oil; second, modern labor-saving appliances reduce the cost of obtaining the oil; and third, the introduction of organized plantation administration with central factories gives great advantages in meeting the market demands. Machinery for the extraction and treatment of palm oil is not of recent invention. Over forty years ago a machine for cracking the nuts and for other purposes was invented, but failed to get acceptance. At present considerable machinery is in use, but definite description of much of it is not available. A bulletin recently issued from the U. S. Department of Commerce gives in considerable detail the nature and operation of the machines recently devised for obtaining palm oil. Palms, as a class, are numerous and include many very useful plants. Their imposing appearance and uses have attracted the admiration of human beings through many centuries. Oils, waxes, fibres, fruits and vegetable ivory enter in commerce in large volume. The West African palm is confined to tropical Africa. The annual export of the oil is estimated at 530,000 tons. In favorable districts, the trees occur in dense forests. Two kinds of oil are obtained from different parts of the fruit. The natives use the oil regularly as an addition to food.

H. L.

IN Bohr's atom of hydrogen, radiation is emitted when an electron displaces itself from one stable orbit to another and the wave-length of the radiation depends upon the location within the atom of the two orbits. When the electron goes from the third to the second orbit the wave-length of the emitted light is $656\mu\mu$, while $486\mu\mu$ and $434\mu\mu$ are the lengths of the waves sent out when the electron goes from the fourth and the fifth orbits, respectively, to the second. From a study of the intensities of these three lines as produced in a Geisler tube the author, who is the director of the Physical Institute of Moscow, has been able to calculate that the number of electrons springing over from the fourth orbit to the second is 25 per cent. of the number passing from the third to the second and that the number going from the fifth to the second is only 17 per cent. of those transferring themselves from the third to the second. "Thus the quantity of springing electrons decreases with the increasing of the distance of the electrons from the centre."

G. F. S.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, June 6, 1923.)

HALL OF THE INSTITUTE,
PHILADELPHIA, June 6, 1923.

MR. W. H. FULWEILER *in the Chair.*

The following reports were presented for final action:

No. 2803: Kingsbury Thrust Bearing. Elliott Cresson Medal to
Albert Kingsbury, Esq., of Philadelphia, Pennsylvania.

No. 2812: Surface Tension Apparatus. Certificate of Merit to Dr.
P. Lecomte du Nouÿ, of New York City, New York.

R. B. OWENS, *Secretary.*

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, June 13, 1923.)

RESIDENT MEMBERSHIP.

ALEXANDER BROWN COXE, Esq., Agriculturist, Paoli, Pennsylvania.

MRS. SELINA EMMA PEACOCK, Organist, 1919 Master Street, Philadelphia,
Pennsylvania.

FREDERICK M. ROONEY, Esq., General Manager, Hiergesell Brothers, 2011
Bellevue Avenue, Philadelphia, Pennsylvania.

NON-RESIDENT MEMBERSHIP.

W. G. H. FINCH, Esq., Radio Editor and Engineer, International News Service,
New York City, New York.

DR. ARCHIE DAYTON POWER, Physicist, University of Minnesota, Minneapolis,
Minnesota.

RICHARD H. RANGER, Esq., Radio Engineer, 66 Broad Street, New York City,
New York.

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BOOK REVIEWS.

LAW CHARTS AND PATENT ENGINEERING. By Harry H. Semmes and Harry R. Van Deventer. 358 pages, 24 charts, 8vo. Washington, D. C., Semmes and Semmes, 1922. Price, \$10.

The authors describe this work as "the first attempt" to present in graphic form the functioning of an engineer attorney, and the procedure before the United States Patent Office and the Federal Courts. The book is thus addressed to that somewhat hybrid profession which combines the functions of the engineer and the lawyer. Dealing, as it does, with procedural rather than substantive matters, it is not believed that it will be of great interest to either of these professions as such. Within the limited class to which it is addressed, the older practitioners will derive little assistance from a work of so general and elementary a character. But to those who are entering upon the profession and to those who contemplate its entry the book will be of very real value. The charts of procedure as elaborated by the text give a compact, integrated view of a subject, the details of which are imbedded in formal rules of practice and other less available sources. That the book has met a very real need for this group is evidenced by the cordial reception given it by the Washington law schools which give special courses in patent law. In several of these institutions the book under review has been adopted as a text on patent procedure.

The vice which this book shares with all manuals, and which its conspicuous merit tends to accentuate, is that it gives an unreal simplicity to its subject. This danger of over-simplification is particularly to be guarded against in books addressed to the novitiates of what may be designated as a dual profession. It suggests to the lawyer a too easy assumption of the functions of an engineer and to the engineer of the attorney's rôle.

Considering more specifically the contents of the book, it will be noted that its subject-matter is broadly divisible into two parts:

1. The scope of engineer attorney's investigations into the originality, patentability and merit of the idea presented to him, and the validity and infringement of patents.

2. The procedure for securing patent protection, i.e., the preparation and prosecution of an application for patent, and the procedure in the Federal Courts for the protection of the right thus secured.

The subject-matter of the first part is not to be found in any work with which the reviewer is familiar and knowledge of it is acquired, as a rule, only in the offices of practitioners. It may be remarked that the present treatment of the subject reflects the viewpoint of the patent department of a great manufacturing concern rather than that of the patent attorney in general practice. The investigations detailed are a little more elaborate than are usually feasible unless relatively large interests are involved and the client can finance extensive researches.

The patent office and court practice charted in the second part of the book finds its source largely in the rules of practice of the patent office in the Federal Equity Rules. These charts are supplemented by forms of pleading carefully selected to illustrate the various procedural steps outlined in the charts.

The only substantive law contained in the volume is an analysis of the relative rights of the employer and the employee in the inventions of the latter made in the course of his employment. This appears in the present volume as an elaborate digression and is unfortunately colored by an apparent bias in favor of the employer.

The outstanding feature of the book is the remarkable clarity and brevity it achieves by the somewhat novel use of charts.

KENNARD N. WARE.

GLUE AND GELATIN. By Jerome Alexander. 8vo, 229 pages, and index. New York, The Chemical Catalog Company. Price, \$3 net.

This is one of the now well-known and much esteemed "Monograph Series" of the American Chemical Society and in form and style agrees with the previous issues. The chemistry and physics of gelatin are complicated problems and are important on account of great industries into which the material enters. Some of the important features of the problems were discussed in this JOURNAL (1922, 194, 564) in connection with Bogue's more extended treatise, and it will not be necessary to repeat them here. Mr. Alexander is an authority in this field and his book will at once take rank as a useful manual. It is of much smaller compass than Bogue's book, but contains a large amount of information on the subject. In the introductory chapter attention is called to the error that is carried through our dictionaries in stating that horns and

hoofs yield gelatin. These portions of the animal yield keratin. Gelatin is obtained from skin and bones. Glue is simply an impure commercial form of gelatin. A frontispiece shows a copy of an Egyptian carving which has been understood as showing the use of glue for joining wood. This picture was also given in Bogue's book with the same explanation, but a note in the present work states that another interpretation of the picture has been made, namely, that the procedure is painting. Alexander does not agree with this view, but the dispute shows how misinterpretations of ancient records may be made.

The book in hand is a compact and comprehensive review of an important subject.

HENRY LEFFMANN.

PLANT PHYSIOLOGY. By Vladimir I. Palladin, University of Petrograd. Authorized English edition based on the German translation of sixth Russian edition with consultation of the seventh (1914) Russian. Edited by Burton Edward Livingston, Ph.D., Johns Hopkins University. Second American edition, with biographic note and chapter summaries by the editor. xxxiii-339 pages, index and 173 illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company. Price, \$4 net.

The problems of plant physiology have been under investigation for many years. They are probably less difficult than those of animal physiology, but as to the fundamental phenomena the basic procedures in both fields are still unknown. What life is, is not yet determined. The tendency for many years has been towards regarding vital action as the operation of the ordinary forces of nature, but many phenomena remain to be explained, and some scientists are still adherents of the theory that vitality is a specific influence. Meanwhile, the great efforts of scientists are directed wisely to collecting facts.

It has for some time seemed desirable to bring the study of plant and animal physiology into one group under the general term "Biology," but this has not been accomplished, and workers in the two fields remain practically indifferent to each other's labors. The work before us is a very comprehensive and detailed statement of the phenomena of plant life in all its bearings. Written in Russian, it would have been of little use to the greater portion of the scientific world, so it is fortunate that it was early printed in German and still better that it has been put into English. Scientists have long been obliged to make themselves tolerably familiar with two languages besides their own, English, French and German having been dominant in scientific literature. Italian has been coming into importance, but it is to be hoped that no condition will arise that will make the acquirement of Slavic tongues necessary to a fair knowledge of current progress.

An editorial note to a brief biography of Professor Palladin, states that the text thereof is taken from the ninth Russian edition, but in the preparation of translation the seventh edition, issued in 1914, was used. A work that has gone through so many revisions may be assumed to have been brought to a highly accurate and comprehensive condition, and an examination shows this to be the case. Yet the editor, who has done his work with great care and attention, has found numerous occasions to amend or even criticize unfavorably the original statements. Scientists who devote themselves for many years to

a narrow specialty are apt to form dogmatic opinions and to propagate them in their writings. Very often the individual ignores the progress of discovery along certain lines, and thus fails to appreciate the error of interpretation and misleads those whom he teaches and for whom he writes. An interesting instance of the blocking of correct teaching is afforded in the case of the respiration of plants. In the middle years of the nineteenth century, the usual teaching was that plants take in carbon dioxide and emit oxygen, reversing the cycle that occurs in animals. Much moralizing was given to this fact as a teleologic relation, it being pointed out that in this way the plant world balanced the animal world and kept the conditions of the air uniform. Yet Boussingault had shown long before that this exchange takes place only in the light, and it was also known that a true respiration similar to that of animals is always occurring in the growing plant. The decomposition of carbon dioxide and elimination of oxygen are more analogous to feeding than to respiration. It has always been an interesting question as to what is the series of chemical changes following the decomposition of carbon dioxide. Baeyer suggested in 1870 that formaldehyde is the first product. A simple equation can be shown by which this substance is formed from carbon dioxide and water, with elimination of oxygen. By polymerization, starch can be obtained without taking up or losing an atom. That starch production is a common process in plants under the influence of light has been well established. Starch by a simple hydrolysis will yield one of the hexoses, which are freely soluble in water, and thus may be rapidly transmitted through the plant cells. It seems that the primary formation of starch is necessary as a storage form, since the soluble sugars would be liable to fermentations. It is, of course, well known that many plants store large quantities of starch, and that these collections are usually associated with one or more catalysts that have the power to accelerate hydrolysis when the vegetable structure is in favorable conditions of heat and moisture. Simple and attractive as the theory of formaldehyde formation and polymerization is, there does not appear to be absolute proof of its truth.

Some considerable changes may be expected soon in the aspects of plant physiology. The importance of the hydrogen-ion concentration has already been emphasized, and it seems likely that a very large part of extensive and laborious work that has been done on soil analysis and the effects of fertilizers will have to be put on the scrap-heap when the data as the hydrogen-ion concentrations of soils have been accumulated in quantity. The problems of plant ecology also open a wide field of investigation. Conditions of association, epiphytism, symbiosis and partial and complete parasitism are widely distributed. Parasitism itself offers an interesting and difficult field extending from the limited relations of species of *Scrophulariaceæ*, *Loranthaceæ* and *Santalaceæ*, through the almost complete dependence of the genus *Cuscuta*, to the banditry of the *Orobanchaceæ*.

The translation is very well done, showing no evidence of either the German or Russian idiom. As Doctor Livingston remarks, western Europe and America have seen Russian literature principally through German or French, and such intermediaries are liable to mislead. It is necessary, therefore, in important matters to go back to the original, which the editor of this book has done. The transliteration of Russian names is one of the difficulties

in dealing with such translations, and, unfortunately, translators do not agree on some of the points. The name of the author of the book is often given as W. Palladin, but it should be V. Palladin, the accent is on the penultimate syllable and no final "e" should be used. A statement of the principles followed with regard to Russian proper names is given in detail.

The book is filled with most interesting biologic information. The literature has been searched with great thoroughness and care and an extensive bibliography is given in the form of footnotes. The editor inclines to some simplification of spelling, but is unfortunately restrained by the conventions in the matter. His scholarship is shown by his calling attention to the fact that "enzyme" should be pronounced with the accent on the first syllable, and he properly observes that the spelling should be without the final "e." He has done well in the matter of bibliographic references, though the reviewer does not like one method adopted. The series number is given in Roman numerals (expressed in Italic capitals), but it would be better to use the now fairly common method of Arabic numerals in brackets, [3], instead of *III*. Efforts should be made to get rid of the Roman numerals. Doctor Livingston has made the proper step in using full-faced Arabic type for the volume number, and it is to be regretted that he did not carry the reform further. It is true that as the series numbers are low, the complexity of the Roman numerals is not in evidence, but in reforming this absurd practice, it would be better to reform it altogether. The mechanical execution of the book is excellent and it constitutes a valuable up-to-date contribution to biology.

HENRY LEFFMANN.

BIBLIOGRAPHICAL HISTORY OF ELECTRICITY AND MAGNETISM, chronologically arranged. Compiled by Paul Fleury Mottelay, Ph.D., with an introduction by the late Sylvanus P. Thompson, D.Sc., F.R.S., and a foreword by Sir R. T. Glazebrook, K.C.B., D.Sc., F.R.S. 8vo, xix-564 pages, frontispiece and plates. Philadelphia, J. B. Lippincott Company, 1922.

This monumental work represents many years of patient, laborious searching of records, musty and recent. The author and the writer of the introduction have both closed their earthly careers, but the book will remain a testimony to their services. The author, of course, deserves by far the greater honor, for the introduction is brief and merely a summary of interesting points. The main portion of the text of the book has appeared in periodical literature, *viz.*, *Engineering*, *The Electrical World*, *La Lumière Électrique* and *L'Industrie Moderne*, respectively, London, New York, Paris and Brussels. In preparation for this book, the texts of these articles have been carefully revised both as to recorded data and literary form, and many new entries added. In addition to the recording of inventions and discoveries, biographical information has been added concerning many of the more prominent workers in the field covered by the book.

Knowledge of some phenomena of electrical action goes back to a remote past. It has long been known that Greek philosophers were familiar with the property of amber acquiring attractive powers by friction, and properties of the lodestone were also noticed at a very early time. When one searches for the initiator of any invention or discovery, it will generally be found that the task is

difficult and it is often impossible to fix the first step definitely. Much careful weighing of evidence and much searching of out-of-the-way tomes are required. The present work is interesting as showing the early date at which the phenomenon of magnetism was apparently known and employed. The date is B.C. 2637, for which several references are given. The item is from Chinese records, and describes the employment of a figure which had the power to point always to the south, so that the army of Hoang-ti was able to pursue an insurgent band through a fog. Notwithstanding the eminent writers from whom this account is quoted, implicit acceptance of such records is hardly advisable, and the date is given without any indication of its possible error. In Greek, Babylonian, Jewish and Egyptian history, dates are very uncertain, and it is scarcely proper that Chinese records going back so far should be accepted without hesitation.

The book is not a history; it is not even a readable volume. It is as unsatisfactory as a dictionary. As a source of material for a comprehensive and valuable history of electricity and magnetism, it will be most valuable, and it is to be hoped that its publication will induce some one to undertake such a history. That work must be done in a critical spirit. The philosophy of history as now in vogue must be applied. It is true that the vast mass of the work done by the workers in this field was without money and without price, so the economic influences which bulk so largely in most human labors do not play a large part here, still it is the duty of the historian to search and set forth the underlying motives in all developments.

Striking, interesting and well-executed plates are included in the volume, and the mechanical character is good with one exception. The binding is much too close, not enough margin being left on the inside of the page. This makes the book difficult to read as it has to be held open with some force. Another fault is the method adopted in the index. This is very full and elaborate, but no indication is given as to the pages on which the more important data concerning a given subject are to be found. In extensive indexes of this character, some pages should be indicated by distinct type so as to facilitate reference to the principal discussion of the subject. The work is a valuable contribution to the literature of the subject.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 157, Nomenclature of Aeronautics. 59 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This "Nomenclature for Aeronautics" was prepared by a special conference on aeronautical nomenclature of which Dr. Joseph S. Ames was chairman. The conference was authorized by resolution of the executive committee of the National Advisory Committee for Aeronautics on January 26, 1922, and the committee officially invited the Chief of the Army Air Service, the Chief of the Bureau of Aeronautics of the Navy Department, the Director of the Bureau of Standards, the Second Assistant Postmaster-General, the Society of Automotive Engineers, the American Society of Mechanical Engineers, and the Aeronautical Chamber of Commerce to designate representatives to serve

on the conference on aeronautical nomenclature. This report supercedes all previous publications of the committee on this subject. It is published with the intention of securing greater uniformity and accuracy in official documents of the government and insofar as possible in technical and commercial publications.

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The Nebular Hypothesis and Modern Cosmogony, being the Halley Lecture delivered on May 23, 1922, by J. H. Jeans. 31 pages, plates, 8vo. New York, Oxford University Press, American Branch, 1923. Price, 85 cents.

Éléments de la Théorie Électromagnétique de la Lumière, par Ludwig Silberstein, ancien professeur de Physique mathématique à l'Université de Rome. Traduit de l'Anglais par Georges Matisse. 93 pages, 12mo. Paris, Gauthier-Villars et Cie., 1923. Price, 6 Francs.

Essentials of Drafting, by Carl L. Svenson. Second edition, revised. 194 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1923. Price, \$1.75.

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THE ELECTRON IN CHEMISTRY.*†

BY

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OXYGEN.

The most fascinating of all magnetic bodies is to my mind oxygen. Here we have one of the simplest of atoms; its atom contains only eight electrons, it is a gas, and therefore in the simplest of all physical states, and yet it alone of all gases is paramagnetic and quite strongly so. Another remarkable thing about it is that innumerable as are the compounds of oxygen there is only one, NO, into which oxygen carries its magnetic properties. This would seem to suggest that the magnetic quality does not arise from some quality intrinsic to the atom, but from some speciality in the arrangement of the colligating electrons in those molecules where it exhibits its magnetic character. The oxygen molecule itself is the most conspicuous example; the arrangement of the electrons may be represented symbolically as two cubes having a face in common, this face being at right angles to the line joining the atoms. If the system were rotating about this line there would be an odd number of square faces in rotation. A rotating square with its electrons would act like

* A series of lectures given before The Franklin Institute, April 9-13, 1923.

† Concluded from the July, 1923, issue, p. 29. "The Electron in Chemistry," 140 pages, 8vo, containing the substance of the five lectures delivered by Sir J. J. Thomson at The Franklin Institute, April 9-13, 1923, will be received from the press on September first. For copies, address The Franklin Institute.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

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a current and thus behave like a magneton. Now suppose that the rotation of electrons must be such that adjacent squares rotate in opposite directions, and it is evident that if we start one from rest in one direction, the adjacent one will start in the opposite direction. Suppose then that the electrons in the planes of the squares were rotating so that the rotation in one plane is opposite to that in the adjacent plane, then two of these planes will be rotating in one direction and the third in the opposite, the resulting magnetic effect will be the same as if only one plane rotated, and this will produce a magnet of finite moment.

It might be thought that if this arrangement of electrons were all that is required to produce paramagnetism, a considerable number of gases would be paramagnetic, whereas so far as is known only two possess this property. The consideration of the arrangement of the electrons in gaseous compounds shows, however, that the configuration of O_2 is almost unique in this respect. Consider the arrangement of electrons in some compounds of oxygen, *e.g.*, in water where it is in combination with two monovalent atoms, the electrons are arranged in an octet which has *two* sets of four electrons in parallel planes, if adjacent sets rotate in opposite directions, the total magnetic effect will be zero. The same is true for a compound like CaO , or for one like CO_2 , where there are four such sets. We see that whenever the oxygen atom occurs, as it always does in valency compounds, with two additional electrons forming an octet, the effect of one face of the octet will always balance that of the other. In a neutral *atom* of oxygen the electrons would be arranged at the corners of an octahedron; if this were to rotate about one of its axes, the four electrons at right angles to the axis would form an unbalanced system and this would have magnetic properties. The magnetic properties of NO , if we take the arrangement of the electrons to be as that given in the first lecture, would arise from the rotation of the three electrons inside the octet, those on the octet itself would not contribute to the magnetic properties. In the compound C_2H_4 we have a similar arrangement of electrons to those in O_2 , but in C_2H_4 all the massive positive charges are not as they are in O_2 on a straight line. The result of this is that if the two octets rotate, say about the line joining the two carbon atoms, they would either have to carry the hydrogen atoms with them, in which case the moment of inertia would be enormously

increased, or else move the electrons relative to the hydrogen atoms; the forces between the positive charges and the electrons would resist this motion, and tend to stop the rotation. In the oxygen molecule the electrons can rotate while the positive parts are at rest. If the compounds NCl or NF existed, the arrangement of the electrons would be as in O_2 , and on the views we have been expressing we should expect that these compounds would be magnetic.

DIAMAGNETISM.

The diamagnetic properties of chemical compounds will furnish, I think, many searching tests of any theory of the distribution of electrons among the atoms of the compound. According to the theory of diamagnetism given by Langevin,²⁹ the contribution of an atom to k , the coefficient of diamagnetism, is equal to $\frac{1}{4} \frac{e^2}{m} \Sigma r^2$. Where $m \Sigma r^2$ represents the moment of inertia of the electrons in the atom about an axis through their centre of figure. The distribution of electrons is supposed to be quite symmetrical so that the moments about all axes are equal, e is the charge and m the mass of an electron.

If n is the number of atoms per unit volume, k , the coefficient of magnetization is given by the equation

$$k = \frac{1}{4} n \frac{e^2}{m} \Sigma r^2 \quad (32)$$

If M is the molecular weight of the system, Δ the density of the substance, N the number of hydrogen atoms in a gram of hydrogen

$$n = \frac{\Delta}{M} N \quad (33)$$

hence

$$\frac{kM}{\Delta} = \frac{1}{4} \frac{e^2}{m} N \Sigma r^2 \quad (34)$$

Thus kM/Δ , which is called the atomic diamagnetic coefficient and is denoted by χ_a , is proportional to Σr^2 , and when χ is known Σr^2 can be calculated. We pass on to consider, what, for our purpose, is the most important application of diamagnetism—the connection between the diamagnetic coefficient of a compound, and those of its constituents.

Pascal³⁰ has made a series of most valuable experiments on this

²⁹ *Annales de Chimie et de Physique* [8], 5, 70 (1905).

³⁰ *Annales de Chimie et de Physique* [8], 25, p. 289.

point, chiefly on organic compounds. He finds that the connection between χ_m , the diamagnetic constant of a compound $A_xB_yC_z$ and χ_a , χ_b , χ_c , the constants for its constituents, is expressed by the relation

$$\chi_m = x\chi_a + y\chi_b + z\chi_c + \lambda. \quad (35)$$

Where λ is a quantity, generally small compared with χ_a , χ_b , χ_c , which depends on the "bonding" of the atoms. Thus, for example, when oxygen is one of the constituents of the molecule, the value of λ , when the oxygen is connected by two linkages with a carbon atom, is not the same as when the oxygen is connected by one link with a carbon and by another to a hydrogen atom; thus, for example, the contributions of the two oxygen atoms in formic acid HCO.OH are different.

Pascal was dealing with valency compounds; in these, on the electron theory, the atom of any particular element will be associated with the same number of electrons whatever may be the compound in which it occurs; thus, for example, the electronegative elements O, S, F, Cl, will always be surrounded by an octet of electrons; the outer layers of the electropositive elements will have been transferred to the electronegative ones to make up their octets. An interesting point arises here in connection with the hydrogen atom and to a less extent with metal atoms. In a compound of hydrogen with an electronegative element, the electron associated with the hydrogen atom has gone to make up the octet round the negative ion, as, for example, in HCl . Thus the hydrogen atom in such a compound is but a positive core, it has no electrons associated with it, and hence on the electron theory of diamagnetism would not contribute anything to the diamagnetic coefficient. Pascal, however, in deducing the coefficient for any compound, assigns to hydrogen a constant value. This is to some extent a matter of bookkeeping, the electrons transferred from the hydrogen to the chlorine will increase the contribution of the chlorine atom to the diamagnetic coefficient. If we like we may transfer this increase to the credit of the hydrogen atom and regard the hydrogen atom as making a contribution to the diamagnetic coefficient, though it does this not by acting itself as the centre of one of the molecular currents, which account for diamagnetism, but by furnishing an electron which increases the molecular currents in some other atom. We should, however,

expect that the amount of the increase would depend upon the kind of atom to which the electron is transferred, that it would increase with the radius of this atom and thus be greater for bromine than for fluorine or chlorine.

We shall now consider what relation would be indicated on the theory we are considering between the diamagnetism of a compound and of its constituents. On the view that, at any rate, in valency compounds there is a transference of electrons from one atom to another, the atoms in the compound are not in the same state as when they were free and uncombined. The atoms of the electronegative elements such as oxygen or chlorine have gained electrons, while those of the electropositive elements have lost them. The coefficient of diamagnetism is proportional to the sum of the moments of inertia of the electrons about an axis through their centre of figure parallel to the magnetic force. If the transference of the electrons involves a change in this moment the coefficient of diamagnetism will be altered by chemical combination, *i.e.*, the additive law will not hold.

Suppose that in the free state the distances of the electrons from the centres of the atoms of the elements A and B are r_a and r_b , respectively, and that the electrons are symmetrically distributed. Then if there are α electrons on A , β on B the coefficient of diamagnetism is proportional to

$$\frac{2}{3} \alpha r_a^2 + \frac{2}{3} \beta r_b^2. \quad (36)$$

If, as the result of chemical combination α atoms are transferred from A to B , if R_b is now the distance of the electrons on the B atoms from its centre the coefficient of diamagnetism is now

$$\frac{2}{3} (\alpha + \beta) R_b^2 \quad (37)$$

This may be written in the form

$$\frac{2}{3} \alpha r_a^2 + \frac{2}{3} \beta r_b^2 + \frac{2}{3} \alpha (R_b^2 - r_a^2) + \frac{2}{3} \beta (R_b^2 - r_b^2) \quad (38)$$

the sum of the first and second terms is the value given by the additive law, the remaining terms represent corrections which must be applied to obtain the diamagnetic coefficient of the compound. If χ_{AB} represents this coefficient, we see

$$\chi_{AB} = \chi_A + \chi_B + \alpha \lambda_{AB} + \frac{2}{3} \beta (R_b^2 - r_b^2) \quad (39)$$

when $\lambda_{AB} = \frac{2}{3} (R_b^2 - r_a^2)$ and is a function which involves the

dimensions of each of the atoms at the ends of the bond binding them together. The term $\frac{2}{3} \beta (R_b^2 - r_b^2)$ depends only upon the atom B , hence the equation may be written as

$$\chi_{AB} = \chi_A + \chi'_B + \alpha \lambda_{AB} \quad (40)$$

where χ'_B depends only upon the properties of the B atom.

Applying the same reasoning to the most general case, we see that λ the value for the compound $A_x B_y C_z$ will be given by an equation of the form $\lambda = x\lambda(A) + y\lambda(B) + z\lambda(C) + \Sigma \lambda_{AB}$.

A term has to be introduced into $\Sigma \lambda_{AB}$ for each electron transferred, *i.e.*, for each valency bond in the compound. Thus we may regard the diamagnetic coefficient of a compound as consisting of a series of terms, one set depending on the atoms in such a way that each atom contributes a definite amount depending only upon the atom; the second set of terms depending on the valency bonds, each bond contributing a term, the value of which depends upon the dimensions of the atoms at the ends of the bond. There may be a term in this set even when the atoms at the ends of the bond are the same; for example, when we have single or double bonds between two carbon atoms: For from the expression for λ we see that they would not vanish unless the radius of the octet round the carbon atoms in the compound $C-C$ was equal to the distance of an electron in a free carbon atom from the centre. As the radius of the octet, round the carbon atoms when there is a double bond $C=C$ is not the same as when there is only a single bond, the value of λ for a double bond is not necessarily twice that for a single one.

Pascal found that a double bond produced a very appreciable *diminution* in the diamagnetism, the magnitude of the effect of the double bond was about equal in magnitude, though opposite in sign to that due to a single carbon atom. The effect of a triple bond was much smaller than that of a double one.

Pascal's researches on the diamagnetism of compounds show that what we have called the λ terms are not in general large compared with the atomic ones, yet these terms undoubtedly exist. He shows, for example, that the contribution of oxygen to the diamagnetic coefficient is not the same, when as in CH_3OH the oxygen is linked by one bond to the carbon and by another to the hydrogen as it is in $CH.O.OH$, where one of the oxygen atoms is linked by two bonds to the carbon atom; he shows, too, that the

contributions of doubly and singly linked carbon atoms are different; he shows in fine that to calculate the diamagnetic coefficient of a compound we must take into account the constitution and configuration as well as the chemical composition.

In addition to the effects produced by the bonding of the atoms, there are others, though probably not so important, arising from what may be called the compressibility of the cell of electrons surrounding the atoms. Thus, for example, it is probable that the distance of the electrons from the centre of the chlorine atoms in HCl is not quite the same as in CCl₄, where the four chlorine atoms may compress each other by their mutual repulsions. A change in the dimensions of the atom would give rise to a change in the diamagnetic coefficient.

The corrections due to the λ terms amount in some cases to as much as 30 per cent., though it is exceptional for them to be as large as this.

From the equation

$$\chi_a = -\frac{1}{4} \frac{e^2}{m} N \Sigma r^2 \quad (41)$$

we can, if we know the value of χ_a , deduce the distance of the electrons from the centre of the atom. For if the distribution of the electrons in the outer layer is symmetrical about the centre

$$\Sigma r^2 = \frac{2}{3} n R^2 \quad (42)$$

where n is the number of electrons in the outer layer and R the distance of these from the centre of the atom; hence

$$\chi_a = -\frac{1}{6} \frac{e^2}{m} N n R^2 \quad (43)$$

or since $e/m = 1.87 \times 10^7$; $e = 1.6 \times 10^{-20}$; $N = 6.16 \times 10^{23}$

$$\chi_a = -3.06 \times 10^{10} \times R^2 \times n. \quad (44)$$

Pascal³¹ gives the following values for $-10^6 \chi_a$.

H	2.93	Al	13.2	As	43	Te	37.5
Li	4.20	Si	20.0	Sc	23	I	44.6
Bc	8.55	P	26.3	Br	30.5	Cs	41.0
B	7.30	S	15	Rb	27.2	Ba	38.2
C	6.80	Cl	20.1	Sr	24.5	An	45.8
N	5.57	K	18.5	Ag	31	Hg ¹¹	33.4
O	4.61	Ca	15.0	Cd	20	Pt	40.3
F	5.95	Cu	18	In >	15	Pb	45.8
Na	9.2	Lu	13.5	Sn ^{iv}	30.3	Bi	192
Mg	10.1	Ga	16.8	Sb ⁱⁱⁱ	74.0		

³¹ *Comptes Rendus*, 158, p. 1895.

From these values of χ_a we find from the preceding equation the following values for the diameters of fully charged electro-negative atoms. The values found by W. L. Bragg³² are given for comparison.

Element.	Diameter from Diamagnetic Constant.	Values Found by Bragg.
O	1.02×10^{-8}	1.30×10^{-8}
F	1.05×10^{-8}	1.35×10^{-8}
S	1.84×10^{-8}	2.05×10^{-8}
Cl	2.0×10^{-8}	2.10×10^{-8}
Se	2.23×10^{-8}	2.35×10^{-8}
Br	2.40×10^{-8}	2.38×10^{-8}
Te	2.8×10^{-8}	2.66×10^{-8}
I	3.0×10^{-8}	2.80×10^{-8}

The agreement between the values of the diameters found from the diamagnetic coefficient and those found by Bragg is fairly close. It is interesting to note that there is nothing exceptional in the value of the strongly paramagnetic element oxygen, from this we conclude that the oxygen atom when it has two additional electrons is not paramagnetic.

When the diamagnetic substance is in a solid state a somewhat different treatment is required. If it is a metal, the electrons will be arranged in lattices and along these lattices the electrons may be free to move. If these lattices form a simple cubical system, then it can be shown that the effect of the electrons on the lattices in a plane at right angles to the magnetic force is to produce per unit area of this plane a magnetic moment equal to $-\frac{1}{16} \frac{He^2}{m}$, when H is the magnetic force, if d is the distance between two parallel lattice planes the moment due to the electrons in unit volume is $-\frac{1}{16} \frac{He^2}{md}$, hence the coefficient of diamagnetism is equal to $\frac{1}{16} \frac{e^2}{md}$.

Since the radius of an electron is of the order e^2/m , we see that the volume coefficient of diamagnetism is of the order of the ratio of the radius of the electron to the distance between adjacent atoms.

³² *Phil. Mag.*, 40, p. 169.

Since the volume coefficient of diamagnetism varies as l/d , and the atomic volume varies as d^3 , we see that for metals of the same valency the diamagnetic coefficient should vary inversely as the cube root of the atomic volume.

ELECTRON THEORY OF SOLIDS.

We shall now proceed to examine how atoms can be bound together not merely in twos or threes to form molecules, but in large numbers so as to form solids. We shall consider how such a collection of atoms is held together and calculate some of its physical properties. We begin with the case when the atoms are all of one kind and when the solid is a crystal, so that it may be regarded as made up of units which are repetitions of each other. These units will be built up of atoms and electrons and the proportion between the number of atoms and the number of electrons will depend upon the valency of the element. Thus for the alkali metals there will be as many atoms as electrons, for the alkaline earths there will be two electrons for each atom, for trivalent metals like aluminum there will be three electrons for each atom and so on. Since the units completely fill space, they must be of the shape of one of the solids into which space may be divided, *i.e.*, the units must be parallelipeda, hexagonal prisms, rhombic dodecahedra or cubo-octahedra.

Let us take the case where the units are cubical. When a number of cubes are built up into a solid each corner of a cube will be the meeting place of eight cubes. Thus, if for purposes of calculation, we take the cube as our unit, and proceed to find the effect of one cube and take the sum of these effects for all the cubes into which the solid is divided, the effect due to an atom or electron at a corner will be counted eight times over. We may compensate for this by assigning to an atom or electron at the corner one-eighth of its normal charge. An atom or electron at the centre of the face of a cube would be common to two cubes and so must be assigned half its normal charge, while an atom or electron at the middle point of a side of a cube will form a part of four cubes and so must be given one-quarter the normal charge.

Thus suppose the atom is at the centre of a cubical layer of electrons, then if the electrons are at the corners of the cube,

both electrons and atoms will be arranged in simple cubical lattices, there will be as many electrons as atoms, the unit cell will be a cube with one-eighth of an electron at each corner and an atom at its centre. Suppose the electrons are at the middle points of the faces of the cube as well as at the corners, there will be four electrons for each atom so that the arrangement will be a possible one for a quadrivalent element. The symmetry of the arrangement shows that it corresponds to a crystal in the regular system. The cell in this case will be a cube with one-eighth of an electron at each corner and half an electron at the centre of each face.

Another quite symmetrical arrangement is when there is an electron at the corner of each cube and one at the middle point of each of its twelve sides; as each side is shared by four cubes the twelve electrons at the middle of the sides will only furnish three electrons to the cell, the one-eighth of an electron at each of the corners will contribute another, so that this arrangement would again be representative of an element in which there are four electrons per atom. The cell in this case will be a cube with one-eighth of an electron at each corner, one-quarter of an electron at the middle point of each side and an atom with a charge four at the centre.

The arrangement of the atoms in each of the preceding cases is that of a simple cubical lattice, the experiments of Sir William and Prof. W. L. Bragg on crystal structures have shown that one of the most frequent arrangements of the atoms is that of face-centred cubes. Here the atoms are at the corners and the centres of the faces of the cubes. If such a cube is taken as the unit cell, one-eighth of an atom must be placed at each corner and half an atom at the centre of each face: This makes each cell contain four atoms. If the atom is one of a monovalent element like lithium, the cell must contain four electrons. These electrons can be arranged with cubical symmetry in two ways—

1. By putting one-quarter of an electron at the middle point of each edge and one at the centre of the cube. This gives an arrangement where each atom has six electrons and each electron six atoms for its nearest neighbours. The atoms and electrons are arranged alternately at equal intervals along the lines of a simple cubical lattice.

This arrangement corresponds to that formed by Sir William and Prof. W. L. Bragg for the chlorides of the alkali metals.

2. Put one electron at the centre of four out of the eight cubes into which the unit cube is divided by planes bisecting the sides at right angles. The four cubes are to be chosen as follows: Take any one and put an electron at its centre, then electrons are to be put at the centres of the three cubes which have an edge but not a face in common with the cube originally chosen. When the cells are put together the same rule must be observed, any two small cubes which have a face in common must have an electron at the centre of one but not at the centre of the other. The four electrons in each cell are at the corners of a regular tetrahedron. The distribution of the atoms and electrons is equivalent to one where each atom is at the centre of a regular tetrahedron of electrons and each electron at the centre of a regular tetrahedron of atoms.

DIVALENT ELEMENTS.

If the atoms in the face-centred cell belong to a divalent element, since there are four atoms in the cell there must be eight electrons.

Two ways in which this may be done are as follows:

1. Fill up the four small cubes which were left empty on scheme 2 for the monovalent elements. Each atom will now have eight electrons as its nearest neighbours, the electrons being at the corners of a cube with the atom at its centre. The cubes surrounding two adjacent atoms have an edge in common and not a face as in the simple cubical arrangement for monovalent atoms.

2. Take the scheme 2 for four of the electrons and in addition place a quarter of an electron at the middle point of each of the twelve sides of the large cube and another electron at its centre.

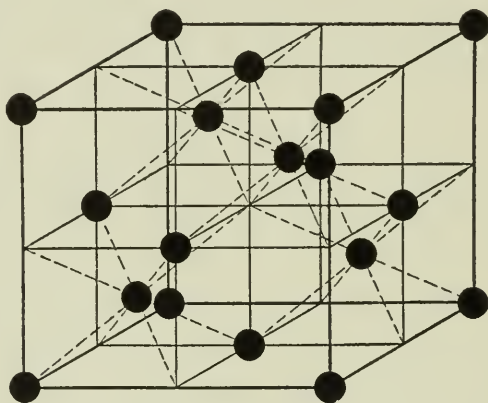
TRIVALENT ATOMS.

When the atoms in the face-centred cube are trivalent there must be twelve electrons in the unit. We can find accommodation for these if we put one at the centre of each of eight small cubes into which the unit cube is divided, a quarter of one at the middle points of each of the twelve edges of the unit cube and another at the centre of this cube. This arrangement is equivalent to putting the atoms at the centres and the electrons at the corners of a series of rhombic dodecahedra filling space.

TETRAVALENT ELEMENT.

The arrangement of the atoms in the diamond has been worked out by the Braggs. It is that shown in Fig. 40. The unit contains eight atoms distributed as follows: One-eighth at each of the corners of the unit, this accounts for one; one-half at the centre of each of the faces, this accounts for three; and four more at the centres of four of the eight cubes into which the unit cube is divided by planes bisecting the sides at right angles. The cubes to be occupied by the atoms are chosen by the same rule as that given for the arrangement of the electrons for the centre-faced arrangement for the monovalent element. As the unit

FIG. 40.



contains eight carbon atoms and carbon is quadrivalent, there must be thirty-two electrons in the unit; these may be arranged as follows:

(a) At the middle points of the sides of the cubical unit; this accounts for three.

(b) At the centre of each of the faces of the eight small cubes; this accounts for twenty-four.

(c) At the centres of the four small cubes not occupied by the carbon atoms; this accounts for four.

(d) One at the centre of the large cube.

Röntgen-ray analysis has shown that for some elements the atoms are arranged at the corners and the centre of a cube. Taking this cube as the unit it contains two atoms; if the element is monovalent, it must contain two electrons. We cannot place these electrons so as to get complete cubical symmetry for one such unit; if, however, we group eight such units together, we get a larger

cubical unit containing sixteen atoms, and it is possible to arrange sixteen electrons in this larger unit so as to get cubical symmetry. Thus we might put pairs of electrons along the diagonals of the eight cubes which go to make up the larger unit.

If the atom were a divalent one we should have to accommodate four electrons in the original unit. This may be done by putting them at the centres of four out of the eight cubes into which the unit may be divided.

HEXAGONAL SYSTEM.

We have hitherto confined ourselves to the consideration of crystals in which the unit was a cube and the arrangement both of atoms and electrons completely symmetrical, so that the crystals would belong to the regular system. If our unit were a hexagonal prism, if, for instance, the electrons were at the corners and the atoms at the centres of hexagonal prisms, then since each corner is common to six prisms, we must, when calculating the electrical forces due to the unit, give to each electron at the corner one-sixth of its normal charge, the twelve electrons at the corners are thus equivalent to two electrons, so that the unit contains two electrons for each atom and would thus correspond to a divalent element.

The arrangement of electrons and atoms in the systems we have described have such regularity that the calculation of the properties of such an aggregate is easier than that of the properties of an aggregate of a small number of atoms in an individual molecule. For the electrons in one part of a molecule, for example, those at the ends of the two octets which form the oxygen molecule, are exposed to forces which are different from those acting on the electrons between the two oxygen atoms. The greater regularity in the arrangement of the electrons in the crystal more than compensates, as far as the mathematical difficulties are concerned, for the necessity of taking into account the effect of a much larger number of electrons and atoms than is necessary for the molecule.

I have in a paper published in the *Philosophical Magazine* (53, p. 721) calculated some of the properties of crystals when the atoms and electrons are arranged according to some of the schemes we have just been discussing. I shall describe the results of these investigations, beginning with the simplest case,

where the atoms and electrons are both arranged in simple cubical lattices, where each atom may be regarded as the centre of a cube formed by eight electrons.

In the paper referred to, the stability of the system is investigated, and it is shown that if $2d$ is the distance between two atoms the arrangement will be stable, provided d is less than $c/1.69$ where c is the distance at which the force exerted by the positive nucleus on an electron changes from attraction to repulsion. As the distance between an atom and the nearest electron is $\sqrt{3d}$, *i.e.*, $1.72d$, we see that for the equilibrium to be stable, the shortest distance between an atom and an electron in the solid cannot exceed by more than a very small amount the distance of the electron from the centre of the atom when the element is in the gaseous state.

The system of electrons and atoms in the metal will have a very large number of periods of vibration, depending on the way the electrons are displaced relatively to each other and to the atoms; the highest frequency of these vibrations is when the electrons are not displaced relatively to each other, but only with respect to the atoms; this corresponds to the displacement which would be produced by light whose wave-length is long compared with the distance between two atoms. I find that this maximum frequency, p , is given by the equation

$$mp^2 = .384 ce^2/d^4 \quad (45)$$

where m is the mass and e the charge on an electron.

If M is the mass of an atom and Δ the density of the solid, then since $8d^3$ is the volume of a cell, $1/8d^3$ is the number of cells in a cubic centimetre, hence

$$\frac{M}{8d^3} = \Delta \quad (46)$$

so that equation (45) may be written as

$$mp^2 = .384 e^2 \frac{8\Delta}{M} \frac{c}{d} \quad (47)$$

This type of vibration is the one that would be excited by waves such as those of visible or ultra-violet light whose wave-length is large compared with the distance between the atoms in the solid. We might therefore expect evidence of it in the behaviour of monovalent metals when acted upon by light, the effect produced upon such metals would be greatest when the frequency of the incident light was that given by equation (45).

An interesting case when the action of light on a metal is a maximum for light of a particular wave-length is what is known as the selective photoelectric effect.³³ This has been measured by Pohl and Pringsheim,³⁴ and in the following table, I give the comparison of the wave-length λ for which the selective photoelectric effect is a maximum for the monovalent metals sodium, potassium and rubidium as determined by Pohl and Pringsheim with the wave-lengths calculated by equation (45) where c/d has been given the value 1.7, *i.e.*, on the supposition that the shortest distance between the atom and the electron in the metal is the same as that in the gas.

Metal.	Δ	$M/1.64 \times 10^{-21}$	λ calculated.	λ observed.
Sodium971	23	3234	3400
Potassium862	39	4457	4400
Rubidium	1.532	85.45	4940	4800

It will be noticed that the agreement between the observed and calculated values is satisfactory.

It is interesting to compare the frequency of this type of vibration of the electrons in the solid, with P , that of the vibration of the electron in a gaseous atom, the latter can easily be proved to be given by the equation

$$mP^2 = e^2/c^3 \quad (48)$$

so we see from (1) if $1.7d = c$ and p is the frequency in the metal

$$p = 1.8P \quad (49)$$

thus the frequency in the metal is a little less than twice that in the gas, the values for the wave-length of the vibrations in the gaseous atom deduced from the table just given are for sodium 5800, and for potassium 7900.

The slowest vibrations of the electrons are when the displacement of adjacent electrons are in opposite directions. Thus suppose one of the lines of the electron lattice is vertical, then the slowest vibration of the electrons is when the electrons in any one line have all equal vertical displacements and the displacements of the electrons in the six vertical lines which are its nearest neighbours are equal in magnitude, but opposite in direction, to that in the line under consideration.

³³ Hughes, "Photoelectricity," Chap. 5.

³⁴ *Verh. d. Deutsch. Phys. Gesell.*, 13, p. 474 (1911).

COMPRESSIBILITY OF THE METALS.

We can calculate the potential energy due to the forces between the atoms and the electrons. I have given the calculations in a paper in the *Philosophical Magazine* (43, p. 721) and have shown that if the metal is supposed to be made up of cubical cells with an atom at the centre and one-eighth of an electron at each of its eight corners, each cell corresponding to an atom with its electron, the potential energy per cell is

$$- 1.825 \frac{e^2}{2d} \quad (50)$$

when $2d$ is a side of the cube. Thus, if there are N cells per unit volume, the potential energy per unit volume is

$$- 1.825 \frac{e^2}{2d} N \quad (51)$$

Now $N = 1/8d^3$, and if as before M is the mass of an atom and Δ the density of the metal

$$NM = \Delta \quad (52)$$

hence the potential energy per unit volume is equal to

$$- 1.825 e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \quad (53)$$

It is shown also that the work required to compress the cells so that the distance between two atoms is reduced from $2d$ to $2(d - \Delta d)$ is equal to

$$1.825 \frac{Ne^2}{2d} \left(\frac{\Delta d}{d} \right)^2 \quad (54)$$

If dV is the diminution in a volume V due to this diminution in d

$$\frac{dV}{V} = 3 \frac{\Delta d}{d} \quad (55)$$

hence the work required to compress the cells in unit volume is equal to

$$\begin{aligned} & \frac{1.825}{9} \frac{N}{2d} e^2 \left(\frac{dV}{V} \right)^2 \\ &= \frac{1.825}{9} e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \left(\frac{dV}{V} \right)^2 \end{aligned} \quad (56)$$

But if k is the bulk modulus, then this work is equal to

$$\frac{1}{2} k \left(\frac{dV}{V} \right)^2 \quad (57)$$

hence

$$k = \frac{3.65}{9} e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \quad (58)$$

The "compressibility" of the substance is equal to $1/k$.

We owe to Professor Richards invaluable determinations of the compressibility of the various elements. The following table contains the results of the comparison of his values of the compressibility with those calculated from equation (58).

Metal.	Δ	$M/1.64 \times 10^{-24}$	k calculated.	k observed.
Lithium534	7	$.14 \times 10^{12}$	$.114 \times 10^{12}$
Sodium971	23	$.068 \times 10^{12}$	$.065 \times 10^{12}$
Potassium862	37	$.03 \times 10^{12}$	$.032 \times 10^{12}$
Rubidium	1.532	85.5	$.022 \times 10^{12}$	$.025 \times 10^{12}$
Cæsium	1.87	132	$.016 \times 10^{12}$	$.016 \times 10^{12}$

Thus the results given by equation (58) are in close agreement with experiment.

If the atoms are in the gaseous state, the work required to change the radius of an atom from r to $r - \Delta r$ is equal to $\frac{1}{2} \frac{e^2}{c} \left(\frac{\Delta r}{r} \right)^2$. Thus to produce the same percentage changes (45) in the sum of the volume of the atoms when in the gaseous state and (47) in the volume of the same number of atoms in the solid state requires the expenditure of amounts of work which are in the proportion of $\frac{1}{c}$ to $\frac{1.825}{d}$, or if $1.7d = c$, of 1 to 3.1. Thus the compressibility of the atoms in the solid state is about one-third of that in the gaseous.

The potential energy of a cell in the solid is equal to $\frac{-1.825e^2}{2d}$ or, since $\frac{1}{(2d)^3} = \Delta/M$, to $-e^2 1.825 \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}$; if M' is the atomic weight of the element

$$M = 1.64 \times 10^{-24} \times M' \quad (59)$$

hence the potential energy of the metal per cell is equal to

$$-e^2 1.5 \times 10^8 \left(\frac{\Delta}{M'} \right)^{\frac{1}{3}} \quad (60)$$

This is equal to the energy acquired by the charge on an electron falling through a potential difference of

$$21.25 \times \left(\frac{\Delta}{M'} \right)^{\frac{1}{3}} \text{ volts.} \quad (61)$$

The values for the various alkaline metals are

$$\text{Li} = 9.25 \text{ volts}$$

$$\text{Na} = 7.3$$

$$\text{K} = 6.36$$

$$\text{Rb} = 5.52$$

$$\text{Cs} = 5.100$$

The work which must be done to pull the cell from the metal and convert it into an atom of a monatomic gas is the difference between the potential energy in the cell and the potential energy of the gaseous atom; the latter when expressed in volts is for a monovalent element equal to the ionising potential.

The potential energy per cell is equal to $-\frac{1}{2}(\tau_1 + \tau_2)$ where τ_1 is the work required to remove a single electron from the metal and τ_2 that required to remove a single atom. We have calculated $\tau_1 + \tau_2$, but not τ_1 and τ_2 individually. If the repulsion between the positive parts of two atoms was proportional to the inverse square of the distance, then τ_1 would be equal to τ_2 , but if the repulsion is equal to $\frac{e^2}{r^2}\left(1 - \frac{cp}{r}\right)$, then τ_2 will be greater than τ_1 , and τ_1 will be less than $\frac{1}{2}(\tau_1 + \tau_2)$. Let $\tau_1 = \frac{\beta}{2}(\tau_1 + \tau_2)$ where β is a fraction, then the work required to remove any electron from the alkali metals will be β times the values given in the preceding tables. The contact difference of potential between two metals is equal to the difference in the amounts of work required to remove an electron from the two metals, thus the contact difference of potential between sodium and potassium would be $\beta(7.3 - 6.36) = .92\beta$ volts. The value found by experiment is .4 volt, hence $\beta = .44$, so that $\tau_1 = .44$ (potential energy per cell).

This gives the following values for the work required to tear an electron from the alkali metals.

Lc	= 4.07 volts
Na	= 3.2
K	= 2.79
Rb	= 2.42
Cs	= 2.24

The work required to tear an electron from sodium was estimated by Richardson from thermionic data as 2.6 volts, and from the photoelectric effect as 2.1 volts. The values given in the table represent the work required to remove an electron from the *body* of the metal; the atoms in the surface layers of the metal differ in energy from those in the interior, and an electron can escape from them with less expenditure of energy. As the values given in the table are less than half the amount of work required to remove both an electron and the positive part of an atom from the

metal, the work required to remove an atom is greater than that required to remove an electron, so that when the metal is heated, the number of positive ions which come off will be small compared with the number of electrons.

The values given on page 161 for the compressibility are for a distribution of atoms and electrons such that the atoms are at the centres of cubes and the electrons at the corners.

When the atoms and electrons are arranged so that atoms and electrons occur alternately at equal intervals along the lines of a cubical lattice, we can show that the electrostatic potential energy for a volume of the metal containing N electrons and N atoms is

$$- 1.77 \frac{Ne^2}{d} \quad (62)$$

where d is the shortest distance between an atom and an electron. If these N atoms and electrons make up unit volume, then if Δ is the density of the metal and M the mass of an atom, since a cube with side $2d$ contains four atoms

$$\begin{aligned} \frac{4M}{8d^3} &= \Delta: \quad NM = \Delta \\ \frac{1}{d} &= \left(\frac{2\Delta}{M} \right)^{\frac{1}{3}} \end{aligned} \quad (63)$$

hence the electrostatic energy per unit volume is

$$\begin{aligned} &- 1.77 e^2 \frac{1}{3} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \\ &= - 2.2e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \end{aligned} \quad (64)$$

It follows from this that the bulk modulus is

$$\frac{2.2e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}, \quad (65)$$

this is not very much more than half the value $\frac{3.65 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$ corresponding to the other distribution which we saw agreed very well with the experiment results; hence we conclude that the atoms and electrons cannot in the alkali metal be arranged so as to occur alternately at equal intervals along the lines of a cubical lattice.

For the arrangement where the atoms are arranged in face-centred cubes with electrons at the centres of four out of the eight smaller cubes into which the face-centred cube is divided, I

find that the electrostatic potential energy for a volume containing N atoms and N electrons is

$$- 3.50 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \quad (66)$$

so that k , the bulk modulus, is equal to

$$\frac{-3.50}{9} e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \quad (67)$$

this differs by less than 5 per cent. from the value given by equation (58), and would agree within the errors of experiments with the values found by Richards.

When the arrangement of the atoms of a monovalent element is that of the body-centred cube and the electrons are placed two by two along the diagonals of eight such cubes taken as a single unit, Miss Woodward finds

$$k = \frac{3.2}{9} e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \quad (68)$$

This would give values for k appreciably smaller than those found by experiment. The arrangement of the electrons was assumed to be as follows: Two electrons were placed inside each cube on a diagonal, one on one side of the centre, the other on the other, midway between the centre of the cube and the ends of the diagonal. The diagonals along which the electrons are placed are chosen so that in a cube built up of eight such small cubes no two of the diagonals in any four whose centres are in one plane are parallel or intersect. The diagonals in two cubes which have a corner but neither an edge nor a face in common are to be parallel. This arrangement is equivalent to arranging the atoms and electrons alternately at equal intervals along lines whose directions are parallel to the four diagonals of the cube.

THE ENERGY AND COMPRESSIBILITY OF DIVALENT ELEMENTS.

We shall further test the electron theory of solids by calculating the compressibility of a divalent element. Calcium crystallises in the regular system and the arrangement of the atoms has been shown by X-ray analysis to be that of the face-centred cube. Taking such a cube as the unit, it contains four calcium atoms; since calcium is divalent, if there are four atoms there must be eight electrons. The most symmetrical way of arranging these is to place one at the centre of each of the eight small cubes into which the unit cube is divided by planes bisecting its sides at right angles.

Taking this arrangement, I find that the electrostatic potential energy of a calcium atom is, if $2d$ is a side of the unit cube,

$$- \frac{e^2}{d} 5.33 \quad (69)$$

while that of an electron is equal to

$$- \frac{e^2}{d} 1.8 \quad (70)$$

Hence the electrostatic potential energy of one atom and two electrons is

$$- \frac{e^2}{d} 8.93 \quad (71)$$

The total actual potential energy, *i.e.*, the potential energy when we take into account the effect of the forces varying inversely as the cube of the distance is one-half of this, *i.e.*,

$$- \frac{e^2}{d} 4.46 \quad (72)$$

Since the cube whose volume is $8d^3$ contains four atoms

$$\frac{4M}{8d^3} = \Delta \quad (73)$$

where M is the mass of an atom and Δ the density of the metal; hence the energy per unit volume is equal to

$$- e^2 5.61 \times \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \quad (74)$$

The bulk modulus k is equal to

$$e^2 \frac{11.2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \quad (75)$$

for calcium $\Delta = 1.55$ and $M = 40 \times 1.64 \times 10^{-24}$, hence k for calcium $= .192 \times 10^{12}$. The compressibility which is the reciprocal of k is 5.2×10^{-12} ; the value found by Richards is 5.5×10^{-12} , so that the agreement between the observed and calculated values is quite satisfactory.

The potential energy for an atom and two electrons is that corresponding to the fall of an electron through twenty-two volts.

THE COMPRESSIBILITY OF A TRIVALENT ELEMENT.

Aluminum is a trivalent element crystallising in the regular system. The arrangement of the atom has been shown to be that of a face-centred cube. Taking this cube as the unit it contains four atoms; it must, therefore, since aluminum is trivalent, contain twelve electrons. If we place electrons at the middle points of the sides, at the centres of each of the eight cubes into which the unit cube is divided by bisecting planes and one at the centre of the

cube, we get a symmetrical distribution of these twelve electrons. This distribution is the same as if each atom were placed at the centre of a rhombic dodecahedron and the electrons at the corners of the dodecahedron. Since four planes meet at some of the corners while only three meet at others, we see that the electrons will be divided into two groups.

For this arrangement I find that the electrostatic potential energy of the atom, with its triple charge of electricity, is equal to

$$-e^2 \frac{10.6}{d} \quad (76)$$

where $2d$ is the side of the face-centred cube and e the charge on an electron.

For an electron at a corner of the dodecahedron where four planes meet, the potential energy is

$$-e^2 \frac{0.5}{d} \quad (77)$$

and for an electron at a corner where three planes meet

$$-e^2 \frac{1.75}{d} \quad (78)$$

Each atom is associated with one electron of the first type and two of the second, hence the electrostatic potential energy of this system is $-e^2 \frac{14.25}{d}$ and the total potential energy $-e^2 \frac{7.12}{d}$.

Now

$$\frac{1}{d} = \left(\frac{2\Delta}{M} \right)^{\frac{1}{3}} \quad (79)$$

hence k the bulk modulus is given by the equation

$$k = \frac{17.8}{9} e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}} \quad (80)$$

for aluminum $\Delta = 2.65$, $M = 27 \times 1.64 \times 10^{-24}$; hence $k = 1.08 \times 10^{12}$, the value found by experiment is $.78 \times 10^{12}$.

COMPRESSIBILITY OF THE DIAMOND.

In the diamond we have a quadrivalent element crystallising in the regular system. The arrangement of the carbon atoms in the diamond has been shown by Sir W. H. Bragg and Prof. W. L. Bragg to be given by the following scheme. The atoms occupy

- (a) the corners of a cube;
- (b) the centres of its faces;
- (c) four of the centres of the eight cubes into which the large cube is divided by planes bisecting its sides at right angles.

We shall take this cube as our unit; it contains eight carbon

atoms. Since carbon is quadrivalent, it must contain thirty-two electrons; these electrons will be situated

- (a) at the middle points of the edges of the cubical unit;
this accounts for three;
- (b) at the centres of each of the faces of the eight small cubes;
this accounts for twenty-four;
- (c) at the centres of the four small cubes not occupied by
the carbon atoms; this accounts for four;
- (d) one at the centre of the large cube.

Making use of this unit, we can calculate the electrostatic potential energy due to the charges on the atoms and electrons. Let E be the charge on a carbon atom, e that on an electron.

The electrostatic potential energy of a carbon atom

$$\frac{1}{2} E \left(\frac{\Sigma e}{r'} - \frac{\Sigma E}{r} \right) \quad (81)$$

I find to be equal to

$$\frac{1}{2} \frac{E}{d} (149.346e - 35.13E), \quad (82)$$

where $2d$ is the side of a unit cube. Since $E = 4e$, this reduces to

$$17.65 \frac{e^2}{d}. \quad (83)$$

The electrostatic potential energy of an electron I find to be

$$\begin{aligned} \frac{1}{2} \frac{e}{d} \left\{ \frac{E}{4} 149.346 - 147.59e \right\} \\ = \frac{1}{2} \frac{e^2}{d} 1.75. \end{aligned} \quad (84)$$

Hence the electrostatic potential energy for the atom and its four associated electrons is $21.15 \frac{e^2}{d}$.

Since there are eight atoms in the cube whose edge is $2d$, if Δ is the density of the diamond and M the mass of a carbon atom,

$$\frac{8M}{8d^3} = \Delta \quad (85)$$

or

$$\frac{1}{d} = \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}. \quad (86)$$

Thus the electrostatic potential energy per one atom and four electrons is

$$21.15e^2 \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}, \quad (87)$$

and the energy per unit volume is

$$21.15e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}. \quad (88)$$

Hence k , the bulk modulus of the diamond, is given by the equation

$$k = \frac{21.15}{9} e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}; \quad (89)$$

for the diamond $\Delta = 3.52$, $M = 12 \times 1.64 \times 10^{-24}$; hence $k = 5.6 \times 10^{12}$, $1/k = .178 \times 10^{-12}$.

This value for $1/k$ is much less than that, $.5 \times 10^{-12}$, found by Richards. It is, however, in close agreement with $.16 \times 10^{-12}$, the value recently found by Adams.³⁵

The properties of solids formed by elements whose atoms have more than four disposable electrons are quite different from those of solids formed by the elements with one, two, or three disposable electrons. The latter are, with the exception of boron, metallic and good conductors of electricity and heat. The former, for instance sulphur and phosphorus, are insulators. Not only do they insulate in the solid state, but they do so after they are fused. They differ in this respect from solid salts which, though they may insulate when in the solid state, generally conduct when melted. This suggests that in the salts there are positively and negatively electrified systems which are fixed when the substance is in the solid state, but can move about when it is liquefied. In such elements as sulphur or phosphorus there does not seem to be any evidence of the existence of anything but neutral systems; in other words, the solid may be regarded as built up of units, each of which contains as much positive as negative electricity. It is noteworthy that according to the Electron Theory of Chemical Combination, two similar atoms, if they have each more than four disposable electrons, like the atoms of sulphur and phosphorus, can combine and form a saturated molecule, which is electrically neutral.

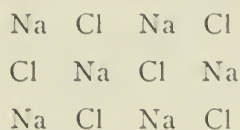
Thus we are led to distinguish three types of solids:

(a) A type where the atoms are arranged in lattices, and the electrons in other lattices coördinated with the atomic ones. In this type each electron has no closer connection with a particular atom than it has with several others. Thus, for example, when the electrons form a simple cubical lattice with the atoms at the centres of the cubes, each electron has eight atoms as equally near neighbours; so that an electron is not bound to a particular atom.

³⁵ *Washington Acad. Sc.*, 11, p. 45 (1921).

This type includes the metals; it also includes boron and carbon in the form of diamond, which are insulators.

(b) A type represented by the salts; here the atoms are again arranged in lattices, but each electron has much closer relation with one particular atom than it has with any other. Thus to take the case of NaCl, where the Braggs have shown the atoms to be arranged according to the following scheme:



We suppose that each sodium atom has lost an electron, while each chlorine atom has gained one; thus each chlorine atom has eight electrons around it, and each electron is much more closely bound to one particular chlorine atom than to any other. It is so closely associated that it is not dissociated from its partner in either the solid or liquid state of the substance. Thus the chlorine system always has a negative charge, the sodium one a positive. These atoms do not move when the substance is in a solid state, though they may do so when it is liquefied.

If the distance of the electrons from the chlorine atoms were to increase until it was not far from half the distance between the sodium and chlorine nuclei, this type would approximate to type (a).

(c) A type where the lattices are built up of units which are not electrified; such units are probably molecules containing two or more atoms, though in certain cases they may be single atoms. The characteristic of the type is that each unit has sufficient electrons bound to it to make it electrically neutral, and that each electron remains attached to a particular atom. Thus where an electric force acts on the system there is no tendency to make the unit move in one direction rather than the opposite, so that the substance cannot conduct electricity.

There is something anomalous about the compressibility of silicon; the arrangement of its atoms as determined by X-ray analysis is the same as that of the diamond, while its atomic volume is 2.7 times greater. We might therefore expect that its compressibility would be (2.7), or 3.8 times that of the diamond. Its compressibility, however, as determined by Richards, is only $.16 \times 10^{12}$, which is practically the same as the revised value for

the diamond. In silicon, however, there are two layers of electrons so that when the four electrons in the outer layer have been distributed to form the lattice, a layer of eight will remain surrounding the positive part of the atom. The compression of the silicon may involve not merely the closer approach of the positive parts of the silicon atoms, but also a closer approach to the central

TABLE VIII.

Potential Energy per Atom with Its Associated Electrons.

Arrangement of Atoms.	K. (Bulk Modulus).
<i>Monovalent Elements.</i>	
CUBICAL	$\frac{3.65 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$
FACE-CENTRED CUBE:	
{ Electrons at middle points of edges and centre of cube	$\frac{2.2 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$
{ Electrons at centres of four constituent cubes	$\frac{3.5 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$
BODY-CENTRED CUBE	$\frac{3.2 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$
<i>Divalent Elements.</i>	
FACE-CENTRED CUBE:	
Electrons at centres of eight constituent cubes	$\frac{11.2 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$
Electrons at centres of edges and four constituent cubes	$\frac{7.75 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$
<i>Trivalent Elements.</i>	
FACE-CENTRED CUBE:	
Electrons at middle points of edges and centre of cube and at centres of four constituent cubes	$\frac{18 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$
<i>Quadrivalent Elements.</i>	
FACE-CENTRED CUBE and at:	
Centres of four constituent cubes. Electrons, centres of edges, centres of faces of constituent cubes and at centres of four of these cubes	$\frac{21.15 e^2}{9} \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$

atom of the layer of eight electrons which surround it. The work required to do this would tend to make the compressibility less than for a substance like carbon, which, after its outer layer has been distributed, has no inner layer left to compress.

The case may be compared with that of a chloride of an alkali metal, say LiCl. In the lattice formed by the atoms each chlorine atom is surrounded by a layer of eight electrons. The compressibility of the salt has been determined by Richards and it is much less than the value calculated on the supposition that the chlorine

ion with its octet of electrons round a positive charge of seven units can be treated as a negative charge of one unit at the centre of the chlorine atom. The compression of the octet round the chlorine atom has also to be taken into account. Miss Woodward has done this recently and finds that the calculated values are in fair agreement with those determined by experiment.

A similar argument applies to the elements copper, silver and gold, which are far less compressible after allowing for the difference in the atomic volume than they would be if they followed the same law as the other monovalent elements, the alkali metals. The heavier alkali metals have also inner layers, but the atomic volume of these is so great that the compression of these layers does not come nearly so much into play as in gold and silver, which have much smaller atomic volumes.

We may sum up the results of the preceding investigation of the compressibility of solids as follows:

The compressibility is equal to $C\left(\frac{\Delta}{M}\right)^{\frac{1}{3}}$, where C is a quantity depending on the valency of the element and the form in which it crystallises; Δ is the density of the solid and M the mass of an atom of the element.

The potential energy of an atom with its associated electrons is equal to

$$- \frac{4.5}{C} \left(\frac{\Delta}{M} \right)^{\frac{1}{3}} \quad (90)$$

Table VIII contains a summary of the preceding results.

SURFACE TENSION.

The preceding expression represents the energy of an atom in the mass of the metal, for one on the surface it requires modification. Thus if P is an atom or electron part of its potential energy depends on the atoms and electrons above a horizontal plane through P . If the metal is broken so that this plane becomes a surface of the metal, the atoms and electrons above P will no longer affect the potential energy so that this will be changed. We can find an approximation to the amount of this change in the following way: Let us take a crystal of a monovalent element and suppose that the atoms and electrons are arranged in the plane of the surface according to the scheme when the atoms are at the corners and centres of the faces of a cube and the electrons at the middle points of the sides and the centre of the cube. This is the

more convenient arrangement to take, since the atoms are present in equal numbers in the plane, so that the total electric charge upon it is zero. With this arrangement I find that the contribution of the atoms and electrons above P to the potential energy of the system consisting of P and an electron is $-.075 \frac{e^2}{d}$, where d is the distance between an atom and the nearest electron. We saw that in this case for an atom and electron in the interior the energy is $-1.77 \frac{e^2}{d}$. Thus the potential energy S of the atom and electron in the surfaces exceeds I , the potential energy in the interior, by $\frac{.075}{1.77} I = .042 I$. The surface tension arises from the excess of the potential energy of the atoms in the surface over those in the interior and is equal to the excess for one atom multiplied by the number of atoms in unit area of the surface. Let us apply this to find the surface tension of sodium. The energy of an atom of sodium not on the surface is equal to that gained by an electron falling through 7.2 volts, *i.e.*, $7.2 \times 1.6 \times 10^{-12}$ ergs. The distance between two sodium atoms is equal to 3.37×10^{-8} , hence the number of sodium atoms per square centimetre is $10^{16}/11.35$. Thus the surface tension of sodium is

$$\begin{aligned} &.042 \times 7.2 \times 1.6 \times 10^4 / 11.35 \\ &= 432 \text{ ergs/cm.}^2 \end{aligned} \tag{91}$$

The value given in the tables for molten sodium is 500, so that the calculated and the observed value are of the same order of magnitude. The calculation is only a rough approximation as we have neglected the effect of temperature and supposed that the distance between the sodium atoms is the same on the surface as in the interior. The increase in the potential energy at a surface will depend upon the orientation of the surface. Thus if the face of the sodium is a plane parallel to the diagonal plane of the cube instead of the plane parallel to one of its faces, I find that the potential energy of an atom and electron at the surface will be greater than if they were in the interior by $.067 I$ instead of $.0423 I$ as in the former case. In this plane the number of atoms per unit area is only $1/\sqrt{2}$ that in the former case, thus the surface tension in this plane will be to that in a plane parallel to a face of the cube in the proportion of 47.3 to 42. The atoms in this plane having greater potential energy than those in a plane parallel to the faces of the cube will

develop a greater amount of heat when they enter into chemical combination. I find that for a gram molecule of sodium the difference would be about 10,000 calories. Thus chemical action would be more likely to go on at these faces than at the natural cleavage faces of the crystal; the photoelectric emission of electrons would also be greater.

COMMUNICATION OF A CHARGE FROM GASEOUS IONS TO THE ELECTRODES.

The preceding values have an important bearing on the transmission of electric charges from gaseous ions to metallic electrodes.

Consider first the case of a positively charged ion. If this is to give up the charge to the electrode and escape as an uncharged atom or molecule, an electron must come from the metal, and be received by the ion. Let the work required to abstract the electron from the metal be V_m and let the ionising potential of the gas be V_g , then the work required to discharge the ion is $V_m - V_g$. If V_m is greater than V_g it will require an expenditure of work to discharge the ion, the ion will not give up its charge, *i.e.*, there will be no continuous current through the gas unless the external potential difference is greater than $V_m - V_g$.

Now take the case of a negatively electrified ion giving up its charge to the anode; here an electron has to be taken from the ion and given up to the anode; to remove the electron requires an amount of energy equal to V_1 , where V_1 is the work required to move an electron from the negatively charged ion, it will be less than the ionising potential. On the other hand, work equal to V_m is gained when the electron goes into the metal thus to effect the transference, work equal to $V_1 - V_m$ must be done, so there must be an external potential difference greater than $V_1 - V_m$ to keep up the current.

It would seem as if experiments on the potential required to effect the passage of electricity from the gas to the metal ought to give us the means of finding V_g and V_1 , quantities which are of fundamental importance in the energetics of chemical combination. To illustrate the kind of effects we are considering, let us take the case of ionised mercury vapour, the ionising potential of mercury vapour is about 10 volts; I cannot find any direct measurements of the work required to extract an electron from liquid mercury, but inasmuch as mercury gives off electrons when exposed to light whose wave-length is not less than 2000, it can-

not be greater than about five volts; thus V_m is much less than V_g ; thus a positively charged mercury atom could give up its charge to a liquid surface of mercury without the aid of an external potential difference. Unless, however, the work required to extract an electron from a negatively electrified mercury atom is less than half that required to extract it from a neutral one, V_1 would be greater than V_m and it would require an external electromotive force to make negatively electrified mercury atoms give up their charge to a mercury surface. Both the gas and the electrode can be varied in these experiments; thus if the gas were a strongly electronegative one, like chlorine, we should expect V_1 to be greater than V_m for a metal like sodium for which Richardson's value is 2.6 volts; if so, it would require an external electric force to make negative chlorine ions discharge to sodium and get free. The chlorine ion would cling to the sodium and combine with it, thus with chlorine ions and an electropositive metal as electrode, the anode would be more likely to be attacked by the chlorine than the cathode. To liberate the electron from the chlorine and get a neutral chlorine atom would require a potential difference at the anode equal to $V_1 - V_m$. At the cathode a positively electrified chlorine atom might not merely get neutralised by receiving one electron, but if V_1 were greater than V_m , work would be gained by the chlorine atom receiving a second electron from the metal. When an electron falls into an atom, light is emitted; the frequency of the light depending on the amount of loss of potential energy caused by the falling in of the atom, or what is the same thing, by the work required to eject the electron again. This work where a positively charged chlorine atom receives one electron and becomes neutral is measured by the ionising potential of the chlorine atom; when a neutral atom receives an additional electron it is measured by V_1 . Thus, whenever, at the surface, say of an alkali metal, the transference of electrons from the metal to, say, chlorine atoms, is going on, light will be emitted; this light will fall upon the metal, and as these metals give large photoelectric effects, it may cause them to emit electrons. As the light is emitted quite close to the surface of the metal, it is quite likely that the intensity at the surface may be sufficient to produce measurable effects though the intensity of the light may be much too faint to be detected at distances large compared with the radius of an atom.

INTERMETALLIC COMPOUNDS.

The expression we have found for the potential energy of a solid has an important application to the theory of intermetallic compounds and alloys. Take the case of two metals, *A* and *B*, when they are apart they consist of lattices of atoms and electrons, and as we have seen may be regarded as built up of units, each unit containing a certain number of atoms, together with the appropriate number of electrons. Thus if the metal were monovalent there would be as many electrons as atoms; if it were divalent there would be twice as many, and so on. Suppose now that the metals were mixed under conditions which permitted free movement of the atoms and electrons. Then in the mixture in addition to the units consisting wholly of *A* or of *B* atoms, we may have units containing both *A* and *B* atoms. Thus to take a definite case, let *A* be sodium and *B* potassium, the unit might be a cube of side $2d$, built up of eight cubes; at the centres of these, atoms of sodium and potassium might be placed alternately, the electrons would be at the corners, the centres of the faces, and the centres of the edges, and at the centre of the large cube. Such a unit would certainly be formed at low temperatures if its potential energy were less than that due to four units of sodium and four of potassium when these metals were separated. Again we might have a cubical unit with the potassium atoms at the corners and the sodium atoms at the centres of the faces; in this unit there would be three sodium to one potassium atom. There are many other possible units with different proportions of sodium and potassium atoms. Whether such units will be formed or not is a question of the relation between the potential energy of such a unit and the potential energy of the atoms it contains when arranged so that the units contain only one kind of atom. The point I wish to emphasize is that the conditions which determine the formation of these metallic compounds are of quite a different kind from those which determine the formation of gaseous compounds containing one or more electronegative constituents. With these it is the valency conditions, such as may be expressed by the formation of octets, which govern the type of admissible compound; with the metals, on the other hand, the formation or not of a compound is determined by the potential energy possessed by a unit of the lattice system formed by the compound. As this potential energy depends on the number of electrons as well as

upon the number of atoms in the unit, and as the number of electrons depends upon the valencies of the atoms, valency will have an influence upon the type of compound, but of a different character to that exerted in compounds between metals and electro-negative elements. From these considerations we should expect that the structure of intermetallic compounds would not conform to the condition of valency as ordinarily understood. We find, for example, many stable compounds in which two atoms of a bivalent metal are combined with one atom of a univalent one, *e.g.*, NaCd_2 , KHg_2 , CuMg_2 , a proportion inconsistent with the usual conception of valency, but one which would be satisfied by a very simple form of unit cell. Thus if the divalent atoms were at the corners of a hexagonal prism and the monovalent atom at the centre, while the electrons were placed at the centres of side faces of the prism and two along the axis on either side of the monovalent atom, we have a unit containing two divalent atoms, one monovalent atom and five electrons.

MIXED CRYSTALS AND INTERMETALLIC COMPOUNDS.

Metallurgists distinguish between two types of combination between metals. The one type called intermetallic compounds consists of alloys of a composition at which on a graph representing the relation between percentage composition and some physical property, such as electrical conductivity, shows a well-marked maximum or minimum. These points in general correspond to alloys in which the proportion between the numbers of atoms of the two metals are expressed by simple ratios. Alloys of other composition represented by the regions between the maxima and minima are supposed to be in a state which is sometimes described as mixed crystals and sometimes as solid solutions.

Let us consider the question of the combination of two metals A and B from the point of view of the electron theory of solids. There are several possibilities, the alloy might be a mechanical mixture of A and B ; by this we mean that the atoms of A and B are respectively arranged in their own space lattices, and that there are no composite space lattices made up of atoms of A and B arranged in regular sequence. Another alternative is that the atoms should be arranged in composite space lattices, the atoms along the lines of the lattices consisting partly of A atoms and partly of B . Here there are again several possibilities, for with a fixed proportion between the number of A atoms and

the number of B there are many different composite lattices possible. Thus, for example, if there are three A atoms for one of B , we might in two dimensional lattices have the spacings

I.

a	a	a	a	a	a	a	a	a
a	b	a	b	a	b	a	b	a
a	a	a	a	a	a	a	a	a
a	b	a	b	a	b	a	b	a

or

II.

a	a	a	b	a	a	a	b	a	a	a	b	a	a	a
a	b	a	a	a	b	a	a	a	b	a	a	a	b	a
a	a	a	b	a	a	a	b	a	a	a	b	a	a	a

or

III.

a	a	b	a	a	b	a	a	b	a	a	b	a	a	b
a	a	a	a	a	b	a	a	a	a	a	b	a	a	a
a	a	b	a	a	b	a	a	b	a	a	b	a	a	b

Thus the alloy might consist either of one kind of lattice or a mechanical mixture of a number of different kinds. If the atoms have been in a condition in which they could diffuse freely, *e.g.*, if the alloy were stirred for a long time when the melt was liquid, the arrangement would be that corresponding to minimum potential energy, remembering that when there is a mechanical mixture of different phases we must take into account the energy due to surface tension. When there is a well-marked minimum in the potential energy for one arrangement of the atoms, we should expect that the alloy would be homogeneous and represented by a single lattice corresponding to this arrangement. If, on the other hand, there are several arrangements which differ but little from each other in potential energy we might expect to find all these arrangements present in the alloy in proportions which would vary with the temperature. When the alloy is homogeneous and the arrangement of atoms and electrons capable of being represented by a single lattice, it corresponds in my view to an intermetallic compound. When, however, there are several different arrangements mixed together, it corresponds to a solid solution.

When the atoms of A and B carry the same charge of electricity, then if A is greatly in excess we should expect the B atoms to occupy positions along a space lattice that differed but little from that for pure A . When, however, the number of the

B atoms increase beyond a certain proportion, there will probably be large modifications in the space lattice for the mixture and possibly the formation of one of quite a different character. The probability of a new type of space lattice will be much increased if *B* and *A* carry different electrical charges, *i.e.*, have different valencies.

Let us consider from this point of view the changes we might expect in the properties of a mixture of two metals, *A*, *B*, starting from pure *A* and ending with pure *B*.

When *A* is greatly in excess, the formation of those compounds which contain a comparatively large proportion of *A* in comparison with *B* will, in accordance with the principles of mass action, be promoted, and the mixture will consist of free *A*, little or no free *B*, and a number of compounds, the majority of which contain an excess of *A* over *B*. As the proportion of *B* increases the amount of free *A* diminishes and the proportion between the amounts of different types of compounds changes, the change being mainly at the expense of those which contain a large number of *A* atoms. When the mixture is such that the proportion between *A* and *B* is that of a possible compound, if that compound is one which has markedly less potential energy than its constituents, the whole mass of metal at low temperatures at any rate may practically consist of this compound. It need not, however, do so in all cases; there may be a certain amount of dissociation of the compound depending upon the temperature. Again, if there is another compound with very small potential energy, some of it is pretty sure to be formed, so that the mixture may not be quite homogeneous even when the proportions are those of a possible compound. When the mixture consists almost entirely of one compound, its constitution is identical in many respects with that of a simple metal. All the units of which it is built up are of one kind, and that kind an arrangement of atoms and electrons, which when the units are united give, as in the cases of metals, a system of lattices for atoms and electrons. Any general property possessed by all metals would, we should expect, be possessed by this compound. In particular the conduction of electricity through the compound would take place by the same mechanism as through metals. Now one peculiarity of the conduction of electricity through metals is that the temperature coefficient of the electrical resistance is much the same for all

metals, hence we should expect that the temperature coefficient of an intermetallic compound would be about that of the pure metals. There seems to be very considerable evidence³⁶ that this is approximately true.

The temperature coefficient of the electrical resistance when the mixture of the two metals contains several compounds is often very much smaller than that for pure metals; in fact, it is even sometimes of opposite sign. When there are several different components the effect of a rise in temperature will be an increase in the dissociation and hence an alteration in the proportion of the amount of different compounds present in the alloy. The more complicated compounds will be split up by the rise in temperature and the proportion of simpler ones increased. As the lattices formed by the complex compounds are more intricate than those of the simpler ones, we should expect their electrical resistance to be greater so that when some of these are split up owing to the rise in temperature there will be a tendency to reduce the resistance. Thus in a mixture of this kind there is, in addition to the normal effect which makes the resistance increase, an effect tending to make the resistance fall when the temperature rises; this will diminish the temperature coefficient of the resistance.

Let us now consider the changes in the elastic properties produced by the formation of these intermetallic compounds. We have seen that in the solid state the potential energy of an atom and its associated electrons is equal to

$$-4.5 \frac{k_A}{N_A} \quad (92)$$

when k_A is the bulk modulus and N_A the number of atoms in unit volume for the element A , since $N_A = \Delta_A / M_A$ where Δ_A is the density of A and M_A the mass of its atom, the potential energy per atom may be written as

$$-4.5 k_A \frac{M_A}{\Delta_A} \quad (93)$$

Thus the potential energy of n atoms of a metal A and m of a metal B before they combine is equal to

$$-4.5 \left(k_A \frac{n M_A}{\Delta_A} + k_B \frac{m M_B}{\Delta_B} \right) \quad (94)$$

³⁶ "Desch. Intermetallic Compounds," p. 52.

If these unite to form the compound A_nB_m , the potential energy per molecule of this compound is

$$- 4.5 \frac{k_{nm}}{\Delta_{nm}} (nM_A + mM_B) \quad (95)$$

Where k_{nm} is the bulk modulus of the compound and Δ_{nm} its density, thus by the formation of the compound, the diminution of potential energy per molecule of the compound formed is

$$4.5 \left\{ \frac{k_{mn}}{\Delta_{mn}} (nM_A + mM_B) - \left(\frac{nk_A M_A}{\Delta_A} + \frac{mk_B M_B}{\Delta_B} \right) \right\} \quad (96)$$

and this must be equal to the heat of formation per molecule of the compound at zero absolute temperature. Thus from the compressibilities of the compound and those of its constituents we can calculate the heat of formation of the compound.

Again

$$\frac{nk_A M_A}{\Delta_A} + m \frac{k_B M_B}{\Delta_B} = K \left(\frac{nM_A}{\Delta_A} + \frac{mM_B}{\Delta_B} \right) \quad (97)$$

and

$$\frac{nM_A}{\Delta_A} + \frac{mM_B}{\Delta_B} = \frac{nM_A + mM_B}{\Delta} \quad (98)$$

Where K is the bulk modulus and Δ the density of the mixture, calculated on the assumption that A and B exert no influence on each other, hence the diminution in potential energy due to the formation of the compound may be written in the form

$$4.5 (nM_A + mM_B) \left\{ \frac{k_{mn}}{\Delta_{mn}} - \frac{K}{\Delta} \right\} \quad (99)$$

Now the compound will not be formed unless the potential energy diminishes, hence $\frac{k_{mn}}{\Delta_{mn}} - \frac{K}{\Delta}$ must be positive, or if, as is generally the case, Δ_{mn} is very nearly equal to Δ , k_{mn} must be greater than K ; in other words, the compound must be less compressible than a mechanical mixture of the metals. It is a general rule that the "hardness" of an alloy is greater than we should expect from its composition, and though hardness is not the same thing as the reciprocal of the compressibility yet some of the tests used to measure the hardness, *e.g.*, the indentation produced by a loaded ball, seem almost more a test of compressibility, the result that combination diminishes the compressibility seems to be indicated.

RADIATION AND CHEMICAL REACTION.*

BY

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THE problem of the emission and absorption of radiation by matter is foremost in the minds of the physicists and chemists of the present day. An exact knowledge of these phenomena implies an exact knowledge of atomic and molecular constitution as well as an exact knowledge of the nature and properties of radiation. Even with such achievements as the Planck radiation formula, the Bohr-Sommerfeld theory of emission spectra, the Debye theory of the atomic and molecular heats of solids in the background, it may be said that only the first steps have been made toward a solution of the problem.

Very closely associated with this development is the obscure and complicated field of chemical reactivity. Every further approximation to exactness in the studies of atomic structure and the nature of radiation premises an advance in a knowledge of the mechanism of chemical reactions, and, *vice versa*, any advances made in the study of chemical reactivity will supplement the knowledge of matter and radiation. In this field, at least, the intellectual interests of the physicists and chemists are identical.

In order to make progress in such a field, it is of great value to have a working hypothesis, founded on the best laws and evidence available, and containing in it ideas, which, whether true or false, possess such a dynamic character as to suggest numerous experiments. The "radiation theory" of chemical reactivity suggested and developed by Trautz, W. C. McC. Lewis, and Perrin, and later further criticized and ramified by Tolman and Dushman, possesses these characteristics. In the following, a brief presentation of this theory and some of its implications will be made.

* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute held Thursday, March 15, 1923.

(1) THE REACTION VELOCITY CONSTANT OF HOMOGENEOUS REACTIONS.

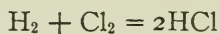
According to the law of Guldberg and Waage, the velocity of a chemical reaction may be expressed by the equation

$$\frac{dm}{dt} = k_1(m_1 m_2 m_3 \cdots m_n) \quad (1)$$

where $\frac{dm}{dt}$ is the velocity at a time t and $m_1, m_2, m_3, \dots m_n$ are the masses of the atomic, molecular, or ionic species present at a time t . When only one species is changing, the reaction is monomolecular, when two species are changing, the reaction is bimolecular and so forth. k_1 is the reaction velocity constant. From the point of view of the student of reaction velocities, it may be said that no two chemical reactions may be expected to have the same velocity constants, and no laws are known which enable the prediction of the numerical value of the velocity constant of an unknown reaction.

Reactions may be divided into two types:

(1) Reactions which have a very high temperature coefficient of reaction velocity constant, or *thermal reactions*, and (2) reactions which have a very low or inappreciable temperature coefficient of reaction velocity, or *photochemical reactions*. An example of a monomolecular reaction of the first type is the thermal decomposition of phosphine in the gaseous phase. An example of a reaction of the second type is a photochemical reaction such as



where visible radiation causes combination and ultra-violet radiation causes decomposition. Incidentally, the rate of decomposition of radioactive elements is a monomolecular reaction obeying the well-known law

$$k_1 = \frac{1}{t} \ln \frac{I_0}{I} \text{ or } I_0 e^{-k_1 t} = I \quad (2)$$

where k_1 is the velocity constant, e is the base of the natural logarithm, I is the radioactive intensity at a time t , and I_0 is the initial intensity. (The intensity is proportional to m , the mass of radioactive substance.) The rate of radioactive decomposition is independent of the temperature, and, consequently, according to the above classification, radioactive changes should be *photochemical*.

Any combination of two molecules to form one or more species is a bimolecular reaction. Thus, the thermal combination of hydrogen and iodine in the vapor phase to form gaseous hydriodic acid is an example. Other familiar examples are the hydrolysis or the saponification of an ester, the hydrolysis of cane sugar, etc.

(2) THE TEMPERATURE COEFFICIENT OF THE REACTION VELOCITY
CONSTANT OF MONOMOLECULAR THERMAL REACTIONS.¹

The velocity constant of a thermal reaction doubles or trebles with a rise of temperature of 10° C. This extraordinary rise in velocity has proved very difficult to explain. Take, for example, any monomolecular reaction, in which one molecular species and only one is changing (the decomposition of phosphine), and consider how a change is brought about. If only the molecules in the reacting chamber and nothing else be taken into account, there are two alternatives: (1) That the molecules decompose spontaneously without being influenced by an external agency; (2) that a molecule decomposes after collisions with other molecules, by means of some kind of molecular shock. Spontaneous decomposition is untenable, because such an assumption involves difficulties in the energy relations, and it would be extremely difficult to explain the increasing explosibility of the molecule with rise in temperature. The theory that the molecule decomposes at each collision with another molecule is also untenable, for, in the first place, it can be shown by kinetic calculations of the change in number of such collisions with the temperature that a rise in 10° C. would only increase the velocity constant about 3 per cent. Substantiating this is the extremely important fact that, at a given temperature, the velocity constant of a monomolecular reaction is independent of the pressure. Further, if molecular shock produced an increase in velocity, the presence of many molecules of an inert substance (argon in the phosphine) would increase the velocity. This, in cases of monomolecular gas reactions, has been shown not to be the case.

In attempting to explain these phenomena, mention should first be made to a simple and brilliant suggestion made by Arrhenius. This was that an ensemble of molecules of any substance at a given temperature contains inactive and chemically

¹ Perrin, *Annales de Physique*, Ser. 9, 11, 5 (1919).

active molecules, and that increase in temperature increases the number of active molecules. It was also shown by Arrhenius that the expression

$$\frac{d \ln k_1}{dT} = \frac{A}{T^2} \quad (3)$$

accounts for the variation of the reaction velocity constant with the temperature in a satisfactory manner. In this equation, k_1 is the velocity constant, A is a constant, and T is the absolute temperature.

In all the previous discussion concerning the monomolecular gas reaction, one very important consideration has been omitted. If a gas is in a hollow space at a given temperature, there is present in this "hohlraum," not only the gaseous molecules but thermal radiation of various wave-lengths and of density corresponding to that temperature. As will be shown in the following section, in considering the kinetics of chemical reactions, not only the mechanism of the reaction but also the mechanism of the radiation, and the exchange of energy between the matter and the bath of radiation must be taken into account.

(3) THE RADIATION HYPOTHESIS OF CHEMICAL REACTIONS.

The idea that radiation is the source of the energy which activates all chemical reactions was first proposed by Trautz.² This point of view has been more clearly stated and generalized by Lewis³ and by Perrin.⁴

Following Perrin, the radiation hypothesis may be stated as follows: "All chemical reaction is provoked by a radiation; its velocity is determined by the intensity of that radiation, and only depends on the temperature in the measure that the intensity depends on it." This statement involves a number of questions of interest. Radiation is here meant in the broadest sense, including all modes of vibration, extending from the extremely short wave-lengths into the longest wave-lengths in the infra-red. In general, visible and ultra-violet absorption or emission is to be associated with the electrons, infra-red absorption or emission

² *Zeits. Photo.*, **4**, 160 (1906); *Zeits. anorg. Chemie*, many articles from 1906 to the present time. See bibliography at the end of this article.

³ *Jour. Chem. Soc.*, numerous articles from 1914 to the present time.

⁴ "Les Atomes," 1913, *Annales de Physique*, (9), **11**, 5 (1919).

with the atoms and molecules. Consequently, purely thermal reactions will be activated by the infra-red. In the second place, the reaction velocity is assumed to be proportional to the intensity of radiation, or the radiation density.⁵ This is the simplest assumption.

According to the above hypothesis, the rate of a monomolecular reaction will be given by

$$\frac{dx}{dt} = \text{constant } (a - x) u_\nu d\nu \quad (4)$$

where x is the mass of substance changed in a time t , a is the initial mass of substance, and $u_\nu d\nu$ is the radiation density. Planck's radiation formula is

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu = \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} d\nu \quad (5)$$

where $u_\nu d\nu$, the radiation density, is the energy density of all modes of vibration with frequencies between ν and $\nu + d\nu$. h is the Planck constant, c is the velocity of light, e is the base of the natural logarithm, k is the gas constant per molecule, and T is the absolute temperature. By means of Fourier series and probability considerations, it can be shown that the number of modes of vibration in unit volume of frequencies between ν and $\nu + d\nu$ is $\frac{8\pi\nu^2}{c^3} d\nu$. According to the quantum theory, the energy

of a mode of vibration of a frequency ν is $\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$. The product

of these two quantities gives the energy of unit volume of radiation of frequency ν . Since π , h , ν , and c are constant, and $d\nu$ is taken for a small finite band of frequencies, the reaction velocity may be written

$$\frac{dx}{dt} = \text{constant } (a - x) \frac{1}{e^{\frac{h\nu}{kT}} - 1} \quad (6)$$

⁵ It is worthy of note that Einstein (*Ann. der Physik*, (4), 37, 832 (1912)), in the deduction of the photochemical equivalent law makes the same assumption that the photochemical reaction rate is proportional to the density of visible or ultra-violet radiation. The radiation hypothesis may, therefore, be regarded as an extension of the Einstein photochemical equivalent law to thermal reactions.

Perrin and Lewis take it that in the infra-red region $\frac{1}{e^{\frac{hv}{kT}} - 1}$ may be put equal to $e^{-\frac{hv}{kT}}$ without making an appreciable error.

The radiation density would also be proportional to $e^{-\frac{hv}{kT}}$ if Wien's radiation formula had been employed. Then

$$\frac{dx}{dt} = \text{constant} (a - x) e^{-\frac{hv}{kT}} \quad (7)$$

Integrating at constant temperature

$$\frac{1}{t} \ln \frac{a}{a - x} = \text{constant} e^{-\frac{hv}{kT}} = k_1 \quad (8)$$

where k_1 is the observed velocity constant. Differentiation of this last equation with respect to T gives

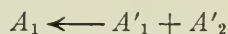
$$\frac{d \ln k_1}{dT} = \frac{hv}{kT^2} \quad (9)$$

Remembering that $k = \frac{R}{N}$, where R is the gas constant per gram molecule, and N is Avogadro's number, we obtain finally

$$\frac{d \ln k_1}{dT} = \frac{Nhv}{RT^2} \quad (10)$$

This important equation has here been derived in a simple manner from the radiation hypothesis with the further assumption of the quantum theory. ν is the frequency which provokes the reaction and is assumed by Perrin and Lewis to be a single frequency or a narrow band of frequencies. To sum up, it is found that by making the velocity constant proportional to the energy density of thermal radiation, an equation similar in form to the equation of Arrhenius may be deduced.

The same reasoning may be applied to polymolecular reactions. Take the reaction



The reaction velocity of combination at constant temperature will be given by

$$v = k' C_{A'_1} C_{A'_2}$$

The temperature coefficient of bimolecular reactions is of the

same order of magnitude as of monomolecular reactions. This large temperature coefficient is not accounted for by the theory of molecular collisions, and, consequently, it is reasonable to assume that the bath of radiation plays a similar rôle in the mechanism of bimolecular and monomolecular reactions.

It is important to know whether v calculated by this equation and observed velocity constants always falls in the infra-red region. This point is confirmed by the following table taken from Perrin's paper:

TABLE I.

Frequencies and Wave-lengths Calculated by Equation (10).

Reaction.	Temperature Range.	$v \times 10^{-14}$	Ångstrom Units.
Saponification of ethyl acetate...	9→45	1.17	25,600
Dissociation of PH_3	310→510	1.2	25,000
$\text{KClO}_3 + \text{FeSO}_4 + \text{H}_2\text{SO}_4$	10→32	1.61	18,600
$\text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I}$	6→30	1.97	15,200
$\text{HPO}_3 + \text{H}_2\text{O}$	0→61	2.0	15,000
$\text{CH}_3\text{CONH}_2 + \text{H}_2\text{O}$	65→100	2.0	15,000
$\text{CH}_2\text{ClCH}_2\text{OH} + \text{KOH}$	24→44	2.14	14,000
Dibromsuccinic acid + H_2O	15→101	2.34	12,800
Diazoaminobenzene → azoaminobenzene	25→35	2.4	12,500
$\text{COS} + \text{H}_2\text{O}$	15→40	2.4	12,500
Inversion of cane sugar	25→55	2.68	11,200
$\text{CH}_2\text{ClCOONa} + \text{NaOH}$	70→130	2.75	10,900
$\text{CH}_2\text{ClCOOH} + \text{H}_2\text{O}$	80→150	2.77	10,800
Dissociation of AsH_3	256→364	2.80	10,000

All wave-lengths correspond to the infra-red region.

(4) INFERENCES FROM STATISTICAL MECHANICS.

It has been shown by Marcelin⁶ and Rice⁷ from considerations of statistical mechanics, that the velocity constant of a thermal reaction will be expressed as a function of the temperature by the equation

$$\frac{d \ln k_1}{dT} = \frac{E_c}{RT^2} \quad (11)$$

⁶ *Comp. Rend.*, 157, 1419 (1913); 158, 116 and 407 (1914); *Ann. de Physique*, (9), 3, 120 (1915).

⁷ *Brit. Asso. Rep.*, 1915, 397.

This equation is of the same form as the equation of Arrhenius and equation (10), but, in this case, a further significance is given to the quantity E_c . Rice showed that E_c equalled the difference between the energy of 1 mol of activated molecules and the average energy of 1 mol of molecules. Tolman⁸ has shown, by a somewhat different mathematical treatment, that

$$\frac{d \ln k_1}{dT} = \frac{\overline{E}_A - E_A + \overline{E}_R - E_R}{RT^2} \quad (12)$$

where \overline{E}_A is the average energy of the molecules which enter reaction, E_A is the average energy of all molecules of this kind, \overline{E}_R is the average energy of the modes of vibration upon entering the reaction, and E_R is the average radiant energy of such modes of vibration whether or not they are in a reactive condition. This equation becomes

$$\frac{d \ln k_1}{dT} = \frac{E_{\text{activated}} - E_{\text{average}}}{RT^2} = \frac{E_c}{RT^2} \quad (13)$$

where E_c , the critical increment, is the energy causing the decomposition of 1 mol of molecules through interaction with "1 mol" of modes of vibration, and E_{average} is the average energy of the molecules and modes of vibration. This latter equation, as well as that of Marcelin and Rice, is of considerable interest because it has been deduced without the assumption of the quantum theory, and the integration has been carried out, not for a narrow range of frequencies, but for all frequencies, and all states of the molecules and modes of vibration. Further, since this equation is similar in form both to the equation of Arrhenius, and to the equation derived by Lewis and Perrin from the radiation hypothesis, it is of considerable value to state, without going into particulars, the assumptions upon which it is based and the method of derivation.

The Maxwell distribution law, which gives the number of elements (molecules or modes of vibration) out of a total number of elements which have coördinates and momenta in an element of volume of generalized space, was deduced by the usual method. The Hamiltonian equations of motion were assumed. The probability of a state described statistically was found, and this probability made a maximum, corresponding to statistical equi-

⁸ *Jour. Amer. Chem. Soc.*, **42**, 2506 (1920).

librium. This involved the use of Stirling's formula for factorials. In applying the Maxwell distribution law to the rate of monomolecular thermal reactions and their temperature coefficients, the following assumptions were made:

(1) The system is gaseous.

(2) The velocity slow and measurable.

(3) Dilute.

(4) Radiation is a necessary part of the reaction. The chance that a molecule will absorb radiation depends on the states of the molecule and the bath of radiation. Thus, the present deduction depends on the radiation theory, but not on the quantum theory.

(5) The integration is to be carried out over all frequencies and all possible states of molecules and modes of vibration. Not a single frequency, or a narrow band of frequency, but all frequencies may cause activation.

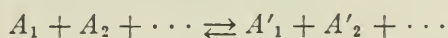
For the temperature coefficient of a truly photochemical reaction activated by a narrow range of frequencies, Tolman obtains the equation

$$\frac{d \ln k_1}{dT} = \frac{\overline{E_A} - E_A}{RT^2} \quad (14)$$

where $\overline{E_A}$ is the energy of the molecules which react and E_A the average energy of the molecules. This temperature coefficient will be very small or perhaps inappreciable.

(5) THE VAN'T HOFF EQUATION.

A chemical reaction represented by



will be in dynamic equilibrium when the velocity from right to left equals the velocity from left to right, and, consequently,

$$v_1 = v'_1 = k_1 c_{A_1} c_{A_2} \cdots = k_2 c_{A'_1} c_{A'_2} \cdots$$

where v_1 , v'_1 , are the velocities from left to right and from right to left, respectively; k_1 and k_2 the velocity constants from left to right and from right to left, respectively, and the c 's represent the concentrations of the molecular species denoted by subscripts. From this equation, it follows that

$$\frac{k_1}{k_2} = \frac{c_{A'_1} c_{A'_2} \cdots}{c_{A_1} c_{A_2} \cdots} = K \quad (15)$$

where K is the equilibrium constant of the reaction.

From statistical mechanical considerations, it has been found that

$$\frac{d \ln k_1}{dT} = \frac{E_{1 \text{ activated}} - E_{1 \text{ average}}}{RT^2} = \frac{E_{c1}}{RT^2}$$

and

$$\frac{d \ln k_2}{dT} = \frac{E_{2 \text{ activated}} - E_{2 \text{ average}}}{RT^2} = \frac{E_{c2}}{RT^2}$$

Since, at equilibrium, $E_{1 \text{ activated}}$ equals $E_{2 \text{ activated}}$,

$$\frac{d \ln \frac{k_1}{k_2}}{dT} = \frac{d \ln K}{dT} = \frac{E_{2 \text{ average}} - E_{1 \text{ average}}}{RT^2} = \frac{\Delta E}{RT^2} \quad (16)$$

It is readily seen that ΔE is the increase in internal energy of the reaction in going from left to right. Equation (16) was first obtained by Van't Hoff by purely thermodynamic reasoning applied to a reaction taking place in a homogeneous system of gases.

(6) SUMMARY AND CONSEQUENCES OF THE PRECEDING DISCUSSION.

From the preceding equations, all the important fundamental equations resulting from the radiation hypothesis may easily be derived.

(1) By the assumption that the velocity of a thermal reaction was proportional to the radiation density, calculated by Planck's formula, the equation

$$\frac{d \ln k_1}{dT} = \frac{N h \nu}{RT^2} \quad (10)$$

has been deduced.

(2) By applying statistical mechanics to the problem of thermal reaction rate,

$$\frac{d \ln k_1}{dT} = \frac{E_c}{RT^2} \quad (11)$$

may be deduced, where E_c is the energy necessary to activate a gram molecule.

From these equations, it follows that if the reaction is stimulated by a single frequency or a narrow range of frequencies,

$$E_c = N h \nu \quad (17)$$

remembering that, by equating these quantities, the quantum theory is tacitly assumed. Equation (17) is an expression of the Einstein photochemical equivalent law for thermal reactions, and states that to produce the decomposition of a single molecule, one quantum of energy, $h\nu$, corresponding to a frequency ν , must be absorbed.

(3) From Van't Hoff's equation and equation (10), the following is obtained

$$\frac{d \ln \frac{k_1}{k_2}}{dT} = \frac{Nh\nu_1 - Nh\nu_2}{RT^2} = \frac{\Delta E}{RT^2} \quad (16)$$

whence

$$\Delta E = Nh(\nu_1 - \nu_2) \quad (18)$$

This formula for the internal energy change of a reaction was originally deduced by Haber ⁹ by a different method. If equation (18) be applied to chemical reactions, then, following the nomenclature of Perrin, all monomolecular chemical reactions should be written in the form

$$Nh\nu_1 + A = A' + Nh\nu_2 \quad (19)$$

where ν_1 is the frequency which activates A causing its decomposition, and ν_2 is the frequency which activates A' and causes its decomposition. Tolman, as previously mentioned, has investigated the case of thermal reactivity where all frequencies may cause activation.

It must be borne in mind that ΔE varies with the temperature. This fact is not explained by equations (18) and (19).

(7) SOME THEORETICAL CONSEQUENCES OF EQUATION (19). PERRIN'S
EXTENSION OF THE RADIATION HYPOTHESIS.

Following the procedure of Perrin, all monomolecular reactions should be written according to

$$Nh\nu_1 + A = A' + Nh\nu_2 \quad (19)$$

A polymolecular reaction would also be written in the same general way, being probably more complicated than the above by reason of the absorption and emission of more frequencies by more molecular species. This equation is regarded as being valid not only for thermal reactions, but for all reactions where the absorb-

⁹ *Ber. Deutsch. phys. Gesel.*, 13, 1117 (1911).

ing or emitting oscillator may be either the atom or the electron. The mechanism of all reactions is therefore fundamentally a universal photochemical mechanism. "All chemical reaction consists of two movements: The absorption of radiant energy which provokes the reaction and the emission of radiation by the reverse reaction." In his admirable defense of this thesis, Perrin has applied the theory to such diverse phenomena as phosphorescence, fluorescence, radioactivity, the evolution of the stars, velocity of crystallization, fusion pressures, sublimation, evaporation, emission and absorption spectra, etc. A few of these examples will suffice to illustrate his method.

(a) *The Quantum Theory*.—When an ensemble of molecules and atoms undergoes a change, the rate of this change can be measured, due to the fact that all the molecules and atoms are not capable of reacting at once. When, however, the change in a single molecule or atom, or the change within a single molecule or atom is considered, the rate of change is extremely great, and immeasurable. From the following postulates, which give a picture of this mechanism, the quantum theory may be deduced:

(1) Matter consists of electrons and positive nuclei, and these elementary oscillators cause the emission and absorption of radiant energy.

(2) These charges are grouped in stable states which do not radiate, and, when in this condition, are atoms and molecules.

(3) Atoms are capable of passing from one stable state to another stable state with great rapidity, thus emitting or absorbing radiation.

(4) The variation of energy is $h\nu$ where ν is the absorbed or emitted frequency and h is Planck's constant.

Thus, a reaction consists of an ensemble of extremely rapid changes from one stable state to another. When a molecule or an atom passes from a stable state a to a stable state a' , $h\nu$ energy is first absorbed by the system in the state a rendering it unstable or active. This absorption will depend on the frequency of oscillation of the atoms or electrons of the system, and the phase, the intensity of the radiation, and, perhaps, some other factors. The unstable state a then changes to the state a' with extreme rapidity, liberating $h\nu'$. The total energy change is $h\nu - h\nu'$. According to Perrin's point of view, there are no exceptions to this picture.

(b) *The Bohr Theory of Emission Spectra.*—If it is assumed, as Bohr assumes, that the atom may exist in a successive series of stable states

$$a_1, a_2, a_3 \cdots a_n$$

possessing internal energies

$$U_1, U_2, U_3 \cdots U_n$$

and that

$$U_n \cdots > U_3 > U_2 > U_1$$

the radiation theory of Perrin falls into accord with the Bohr theory. For let each of the stable states correspond to definite electronic arrangements, electronic orbits. Then, if an electron passes from a_5 to a_3 , the energy emitted is according to the Bohr theory

$$U_5 - U_3 = h\nu'$$

It is hard to understand this spontaneous change or jump from one stable state to another without the agency of an external stimulus. The application of the fundamental equation

$$\overrightarrow{h\nu} + A \longrightarrow A' + \overrightarrow{h\nu'}$$

removes this difficulty. Thus, light of a frequency $\frac{U_5 - U_2}{h}$ may transform an atom from a state a_2 to a state a_5 . If the electron then falls into an inner orbit, or a state a_3 , the frequency $\frac{U_5 - U_3}{h}$ would be emitted. This whole process may be written

$$h\left(\frac{U_5 - U_2}{h}\right) + a_2 \longrightarrow a_3 + h\left(\frac{U_5 - U_3}{h}\right)$$

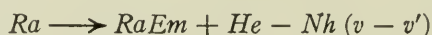
(c) *Radioactive Transformations.*—Since equation (19) is held to be valid for all transformations of matter, it should be valid for radioactive decompositions. Radioactive changes apparently take place spontaneously according to the law of monomolecular change. The rate is independent of the temperature and all other external conditions. At first glance these changes are like explosions, taking place with an enormous evolution of heat. Radioactive change has thus always been supposed to be exothermic.

Perrin assumes that the decomposition of radioactive atoms is not exothermic but endothermic, and is produced by the absorption

of radiations of very high frequencies ($\nu = 10^{21}$ or 1000 times the frequencies of X-rays). These rays traverse all substances, and are formed in the incandescent centre of the earth. Radiation of such frequency will not exist in ordinary thermal radiation, and thus radioactive decomposition will be independent of the temperature. The process may be expressed by



where ν is radiation of this enormous frequency, and ν' is the frequency of the thermal radiation emitted. From the above equation



and, consequently, the reaction takes place with the absorption of energy equal to $Nh(\nu - \nu')$. In this ingenious way, the theory may be applied to radioactive phenomena, and the difficulty of explaining spontaneous explosibility avoided.

(8) THE EINSTEIN PHOTOCHEMICAL EQUIVALENT LAW.

The Einstein photochemical equivalent law may be stated as follows: If a gram molecule of any substance is decomposed by luminous or ultra-violet radiation of frequency ν , $Nh\nu$ radiation energy must be absorbed by the substance. This law was originally deduced by Einstein for purely photochemical reactions by a method quite different from the method employed in the present discussion. In Einstein's deduction, however, the same fundamental assumption as that underlying the radiation hypothesis, namely, that the reaction rate of a photochemical reaction is proportional to the density of the radiation absorbed. This assumption, which is the simplest, is made in all these theories.

Many investigations of photochemical reactions reveal that for certain reactions which Bodenstein¹⁰ has conveniently called primary reactions, the photochemical equivalent law holds within the limit of experimental error. In Table II are given a few examples selected from the collection of data presented by Bodenstein and Dux.

¹⁰ Bodenstein and Dux, *Zeits. Physik. Chem.*, **85**, 297 (1913).

TABLE II.
Primary Photochemical Reactions.

Reaction.	Absorption.	Law of Velocity.	$\frac{h\nu}{\text{Molecule}}$
$3\text{O}_2 = 2\text{O}_3$	Weak	$k_1 (\text{O}_2)$	4
	Strong	k_1	
$2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$	Strong	k_1	1 for 2 NH_3
Anthracene \longrightarrow dianthracene	Medium	$k_1 I$	0.7 \longrightarrow 1.0
$S_\lambda = S_u$	Medium	$k_1 I$	4 \longrightarrow 5 (approx.)

(I is the light intensity; (O_2) is the concentration of oxygen molecules.)

These results are of the right order of magnitude, and, since any direct method of measuring the energy absorbed is difficult, may be considered as good evidence for the law. In these reactions, the equivalence of the exchange of energy between the radiation and matter appears to be established.

There are, however, a class of reactions, secondary light reactions, which are exceptions to the photochemical equivalent law. A few examples, selected from Bodenstein's and Dux's paper, are given in Table III.

TABLE III.
Secondary Photochemical Reactions.

Reaction.	Law of Velocity.	$\frac{\text{Molecules}}{h\nu}$
$\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$	$\frac{k_1 (\text{Cl}_2)^2}{(\text{O}_2)}$	10^6
$2\text{O}_3 = 3\text{O}_2$	$\frac{k_1 (\text{O}_3)^2}{(\text{O}_2)}$	$10^2 \longrightarrow 10^3$
$4\text{HI} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{I}_2$	$k_1 [\text{I}_2] [\text{O}_2]$	10^6
$\text{Br}_2 + \text{C}_7\text{H}_8 = \text{C}_7\text{H}_7\text{Br} + \text{HBr}$	$k_1 [\text{Br}_2] [\text{C}_7\text{H}_8]$	10^6

In three of the above reactions, for 1 $h\nu$ absorbed, 10^6 molecules react.

Notable attempts have been made by Bodenstein and Nernst to explain this enormous discrepancy. Bodenstein's theory was based on an assumed photoelectric effect on the molecules. Nernst¹¹ admits that all primary photochemical reactions conform to the Einstein photochemical equivalent law. In the case

¹¹ *Zeits. Elektrochemie*, 24, 335 (1918).

of secondary light reactions, secondary reactions of an obscure nature take place. Nernst explains the photochemistry of the reaction of formation of hydrogen chloride from hydrogen and chlorine as follows:

(1) The primary reaction which obeys the Einstein law is



(2) Two secondary reactions take place simultaneously, which are



According to the above processes, from an extremely small number of chlorine atoms, a relatively large number of hydrogen chloride molecules may be formed. This explains also why this reaction is retarded by the presence of traces of impurities such as ammonia.

The primary light reaction liberates atoms. If there is present in the system "acceptors" or molecules easily capable of reaction with these atoms, very many molecules may be formed per quantum of light absorbed. If there is no acceptor present, fewer molecules may react than required by the photochemical equivalent law. This point is in accord with the experiments of Pusch¹² on the reactions between hydrogen and bromine and hexahydrobenzene and bromine.

All the above examples refer to true photochemical reactions brought about by the absorption of visible or ultra-violet light. No direct evidence of the kind has been contributed for the establishment of the law for reactions stimulated by infra-red radiation. The behavior of thermal reactions may be proved to be quite different.

(9) DUSHMAN'S THEORY.¹³

From statistical mechanical and thermodynamic theory, it has been found that

$$\frac{d \ln K}{dT} = \frac{\Delta E}{RT^2} = \frac{E_1 - E_2}{RT^2} \quad (16)$$

and

$$\left. \begin{aligned} \frac{d \ln k_1}{dT} &= \frac{E_1}{RT^2} \\ \frac{d \ln k_2}{dT} &= \frac{E_2}{RT^2} \end{aligned} \right\} \quad (11)$$

¹² *Zeits. Elektrochemie*, **24**, 336 (1918).

¹³ *Jour. Amer. Chem. Soc.*, **43**, 397 (1921).

K is the equilibrium constant of the reaction, ΔE the heat of reaction, k_1 is the velocity constant in one direction, k_2 the velocity constant in the reverse direction, and E_1 and E_2 are the heats of activation per mol. Before a reaction can occur in one direction or the other, the molecules must have acquired an energy E_1 or E_2 in excess of the average energies of the molecules. The fraction of the total molecules, N , which have acquired this energy may be calculated by means of the Maxwell distribution law for energies. Thus, the number of molecules dN_E which possess an energy between E and $E + dE$ is given by the equation

$$dN_E = \frac{N}{E_0} e^{-\frac{NE}{RT}} dE \quad (20)$$

If N is Avogadro's number, R will be the gas constant per mol. Let the mean initial energy of 1 mol of the molecules be E_{average} and let this energy be increased to the critical value E by the amount E_1 by the absorption of "1 mol" of radiation. The fraction α_E of the molecules which have a critical energy E will be given by

$$\alpha_E = \frac{\int_E^\infty \frac{N}{E_0} e^{-\frac{E}{RT}} dE}{\int_0^\infty \frac{N}{E_0} e^{-\frac{E}{RT}} dE} = \frac{-RT e^{-\frac{E}{RT}} \Big|_E^\infty}{-RT e^{-\frac{E}{RT}} \Big|_0^\infty} = e^{-\frac{E}{RT}}$$

Likewise, the fraction, $\alpha_{E_{\text{average}}}$, of the N molecules which have an energy E_{average} , will be

$$\alpha_{E_{\text{average}}} = e^{-\frac{E_{\text{average}}}{RT}}$$

Then the fraction, $\alpha_E - \alpha_{E_{\text{average}}}$, which have received the energy E_1 will be

$$\alpha = e^{-\frac{E}{RT}} - e^{-\frac{E_{\text{average}}}{RT}} = e^{-\frac{(E - E_{\text{average}})}{RT}} = e^{-\frac{E_1}{RT}} \quad (21)$$

If the reaction velocity constant, k_1 , is assumed to be proportional to α , the equation

$$k_1 = \nu e^{-\frac{E_1}{RT}} \quad (22)$$

is obtained. k_1 has the dimension of t^{-1} or a frequency. The quantity E_1 has been shown to equal $Nh\nu_1$, the energy acquired

by the absorption of a frequency ν_1 . Therefore

$$k_1 = \nu e^{-\frac{N h \nu_1}{RT}} = \nu e^{-\frac{h \nu_1}{kT}} \quad (23)$$

where $k = \frac{R}{N}$, an equation similar to equation (10).

Dushman's theory rests on the following assumptions:

- (1) ν in equation (23) is a frequency.
- (2) The relation $E_1 = N h \nu_1$ is valid.
- (3) Dushman finally makes the bold assumption that

$$\nu = \nu_1 = \frac{E_1}{N h} \quad (24)$$

As a result of the above considerations and assumptions, the velocity of a monomolecular reaction will be given by

$$-\frac{dc}{dt} = c \nu_1 e^{-\frac{h \nu}{kT}} \quad (25)$$

and the velocity constant by

$$k_1 = \nu_1 e^{-\frac{h \nu}{kT}} = \frac{E_1}{N h} e^{-\frac{E_1}{RT}} \quad (26)$$

If the reaction be carried out at constant volume, E_1 will equal Q_1 , the heat of activation, and thus Dushman's equation for the velocity constant of a monomolecular reaction is

$$k_1 = \frac{Q_1}{N h} e^{-\frac{Q_1}{RT}} \quad (27)$$

Dushman has been able to show that this equation accounts for the present available data with considerable accuracy. Herein lies the justification of his assumptions. In the following, a calculation of the velocity constant of the dissociation of phosphine, taken from Dushman's paper, is given.

$$N = 6.062 \times 10^{23}$$

$$h = \frac{6.55 \times 10^{-27}}{4.184 \times 10^7}$$

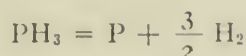
Hence from equations (25) and (27)

$$k_1 = -\frac{dc}{cdt} = 1.048 \times 10^{10} Q_1 e^{-\frac{Q_1}{RT}}$$

or

$$\log k_1 = 10.0203 + \log Q_1 - \frac{Q_1}{4.571T} \quad (28)$$

The velocity of the reaction



has been studied by Trautz and Brandharkar¹⁴ and the reaction rate has been shown by them to be free of catalytic effects which might be produced by the walls of the vessel. The observed and calculated values are shown in Table IV. Under k_1 (obs.) are the values taken from the data of Trautz and Brandharkar. Under k_1 (graph) are the values read off the smooth plot of the velocity constants against the absolute temperature. Q_1 (calc.) was computed by means of equation (28), and k_1 (calc.) was obtained by means of the same equation from the mean value of Q_1 or 72,500 cal.

TABLE IV.

T.	$10^3 k_1$ (obs.)	$10^3 k_1$ (graph)	Q_1 (calc.)	$10^3 k_1$ (calc.)
956	22; 11; 22	18.3	72,760	17.5
953	15; 11	15.0	72,740	15.2
948	17; 10; 10; 11	12.0	72,710	12.4
945	8.5	10.2	72,760	10.8
942	17	9.1	72,780	9.6
940	13; 14	8.3	72,740	8.9
936	2.7; 3; 8.3; 7.6; 8.7	7.1	72,730	7.6
933	12	6.3	72,690	6.6
929	5.6	5.5	72,610	5.6
923	4.4	4.6	72,560	4.4
918	3.6	3.8	72,520	3.5
845	0.54		69,920	0.113
785	0.0021			0.0041
719	0.00081			0.000055

The constancy of Q_1 (calc.), and the agreement between the calculated values of k_1 and the values read off the plot afford an interesting confirmation of Dushman's contentions.

In the remainder of Dushman's paper, the same method has been applied in calculating bimolecular velocity constants and also equilibrium constants of various reactions. The agreement between the observed and calculated values is indeed remarkable, but further discussion at this point would be beyond the scope of the present survey.

¹⁴ *Zeits. anorg. Chem.*, **106**, 45 (1919).

(10) GENERAL CONSIDERATIONS AND CONCLUSION.

The present brief presentation of the hypothesis which makes radiation the cause of chemical reactivity by virtue of the power of radiation to bring molecules or atoms into an active state makes no pretention of being consistent throughout. There are important differences in the theories of those who have contributed to this field. However, all are agreed that the bath of radiation in which the reacting substances are placed is of fundamental importance in the mechanism of chemical reactions.

Lewis and Perrin have based their theory on the assumption that the energy activation is due to the absorption of radiation of a narrow range of frequencies. For thermal reactions, these frequencies occur in the infra-red region. Langmuir¹⁵ has raised two important objections to this point of view. Firstly, since the reacting substance must absorb radiation of a given frequency, the substance should exhibit an absorption band corresponding to that frequency. He points out that in numerous cases there is no evidence of such bands. Secondly, the energy necessary to activate phosphine at 948° C. is 4×10^{10} greater than can be obtained from the radiation (frequency 392 $\mu\mu$; calculated by the radiation hypothesis as the frequency of activation of phosphine) of a black body at that temperature.

Lewis and McKeown¹⁶ have attempted to answer these criticisms. They emphasize the important difference between a true photochemical reaction and a thermal reaction. In a photochemical reaction, the temperature of the reacting system is very different from that of the radiation, while in thermal reactions, there is thermal equilibrium between the radiation and the reacting system. Thus, in the latter case, when energy corresponding to a narrow range of frequencies is removed by the reacting system from the bath of radiation, thus disturbing the equilibrium, the bath will tend to restore equilibrium (if maintained at a constant temperature), and more modes of vibration of the required frequency will be produced, thus supplying the necessary energy.

Tolman, by adopting the fundamental different point of view that for thermal reactions all frequencies may stimulate the reacting system, offers another method by means of which Langmuir's objections may be removed. Certainly, not enough data have been

¹⁵ *Jour. Amer. Chem. Soc.*, **42**, 2190 (1920).

¹⁶ *Jour. Amer. Chem. Soc.*, **43**, 1288 (1921).

accumulated to definitely settle whether a narrow band, all frequencies, or all frequencies beyond a threshold frequency are responsible for thermal reactivity.

The radiation theory at present marks the beginning of a new interpretation of chemical reactivity, and should be considered as a step towards the solution of this different problem, not a valid solution. The spirit of approach may best be realized by a quotation from Perrin, who is one of the masters in this field. "J'ai tenté de montrer qu'on développer une theorie cohérente qui voit dans la lumière la cause des reactions chimiques, et qui élucide et rapproche des classes étendues de phénomènes au premier abord assez dissemblables. Dissociations ou combinaisons, phosphorescences, radioactivité, changements d'état physiques, semblent obéir à une même loi fondamentale par où se traduit, à notre echelle, la physique intérieure à l'atome. Je ne me dissimule ni la caractère préliminaire d'une étude qui n'est encore que grossièrement approchée ni les incertitudes ou les difficultés qui subsistent, et surtout je sais la nécessité de faire des experiences dont certaines sont suggérées avec evidence. Mais le travail sera peut-être considerable et j'ai cru pouvoir indiquer les principes qui le dirigeront."

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On Some Alpha Ray Tracks. C. T. R. WILSON. (*Proc. Cambridge Phil. Soc.*, vol. xxi, part iv.)—Four splendid photographs are reproduced of the tracks of alpha rays from thorium or one of its descendants. It is remarkable how Mr. Wilson can explain just how the idiosyncrasies of the paths came about. His is a powerful method.
G. F. S.

THE MODIFICATION OF WIND-TUNNEL RESULTS BY THE WIND-TUNNEL DIMENSIONS.*

BY

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SUMMARY.

THE necessary corrections are determined for the influence of the dimensions of the wind-tunnel upon the results of tests on wings and propellers.

Tests for the investigation of this question have probably been made in every wind-tunnel. The problem is indeed of great importance, whether the influence of the boundaries of the air current can be neglected or not. In the former case the investigator should, whenever possible, clearly and distinctly realize how much he neglects. The application of a correction, on the other hand, enables him to compete successfully with a tunnel of much larger dimensions, where the models have to be kept smaller than is really necessary because the testing engineer is ignorant of the necessary corrections. Here it becomes manifest that an able and well-informed engineer is able not only to increase the efficiency of his wind-tunnel in general, by selecting, arranging and interpreting the tests, but even to increase the effective capacity of his tunnel.

The question of the influence of the dimensions of the wind-tunnel is by no means difficult. I hope that this note will enable every wind-tunnel engineer to become sufficiently acquainted with the present state of this part of aerodynamics. There is a primary and a secondary effect. The theoretical flow of a perfect fluid inside a tunnel does not agree exactly with that in an unlimited space. The difference gives rise to a change of the pressures and of the air forces. In addition it gives rise to a change of the modifications of the theoretical flow caused by viscosity. This again changes the pressures and forces. Only on the former

* Communicated by Dr. Joseph S. Ames, Director, Office of Aeronautical Intelligence, National Advisory Committee for Aeronautics and Associate Editor of this JOURNAL.

influence is exact information available at present. This influence is by far the more important one in most cases.

The modification of the results depends entirely on the type of tunnel, whether (*a*) the air current flows within a tube in contact all around with the solid walls thereof, or whether (*b*) the air current in the zone of testing is a free jet, in direct contact all around with air virtually at rest. The solid wall restricts the free motion of the adjacent particles of air, reacting with such force as to constrain them to flow parallel to its surface, so that the velocity component at right angles to the wall is always zero. The motion of the free jet, on the contrary, is not directly restricted, the surrounding air allowing any shape of the jet. The surrounding air, however, being at rest, exerts the same pressure along the entire surface of the jet. Hence the motion inside the jet is determined by the condition that the pressure on the surface becomes constant.

WING TESTS.

For each of these two wind-tunnel types, the chief kinds of experiments have to be investigated separately. The correction for wing tests in both kinds of tunnels has been given in a complete and correct form by L. Prandtl.¹ I am afraid, however, that his arguments, though absolutely clear and convincing to every mathematician, will not be understood readily by many of his readers who are less mathematically trained. I proceed therefore to repeat the arguments in a much simplified way, making no use of any vortices, but only of the chief characteristics of each aerodynamic flow, *vis.*, its momentum and its kinetic energy.

A wing moved through air produces a distribution of velocities having components in all directions. The investigation is simplified by considering separately the structure of the flow near the wing and the general characteristics of the entire flow. With respect to the flow near the wings it can be assumed that the velocities have no transverse components, *i.e.*, parallel to the span of the wing, so that each longitudinal vertical layer of air remains plane. With respect to the general characteristics of the flow, on the contrary, it can be assumed that the flow has no longitudinal component, so that all transverse vertical layers of air remain plane. The superposition of these two flows gives the final result with sufficient accuracy.

The flow surrounding the wing can not be directly influenced by the walls of the tunnel. The change of this flow is indirectly brought about by the change of the general characteristics of the flow. Hence the present investigation has as its object the two-dimensional distribution of flow in the transverse vertical layers. Each particle of air in the layer is supposed to have originally no velocity components at all parallel to its plane. When approaching, passing and leaving the wing behind it, a transverse two-dimensional distribution of flow is gradually built up in each layer. The momentum of the air downward transferred to the layer with the thickness equal to the velocity V is equal to the lift L . The kinetic energy of the flow in this layer when finally built up depends on the longitudinal projection of the wing or wings and on the distribution of the lift over the wings. It may be denoted by P . This kinetic energy can be assumed to be concentrated in a fictitious quantity of air $K\rho V$, moving with constant downward velocity u and having the momentum L received from the wing. It will be noticed that K has here the dimension of an area, the area of the apparent mass of the front view of the wing. The induced drag has to absorb the energy P necessary to create the flow. This is expressed by the equations,

$$P = KV\rho \frac{u^2}{2} \qquad L = KV\rho u$$

Therefore

$$D_i = \frac{P}{V} = \frac{L^2}{4V^2 \frac{\rho}{2} K}$$

The resultant air force has the average inclination towards the vertical

$$\alpha_i = \frac{D_i}{L} = \frac{L}{4V^2 \frac{\rho}{2} K}$$

These conclusions remain correct whether the air current is unlimited or bounded by the walls of the wind-tunnel. In the latter case, however, the transverse flow is modified and hence its apparent area of mass K , too. The problem is thus reduced to the determination of the apparent mass K' inside a tunnel, if the apparent mass K under the same conditions in unlimited air is known.

The exact solution depends not only on the area of the apparent mass, K , but on the exact distribution of the lift and on the shape of the wind-tunnel section. For the present purpose, however, it is exact enough to solve the problem for one particular condition, chosen so as to make the solution as simple as possible, and to assume that the result holds good for any other case with equal area K and area S' of the wind-tunnel section. The particular problem, easy to be computed, is an arrangement of wings like Venetian blinds, a multiplane, as it were, of an infinite number of wings, in front view in the form of a circle, and with such distribution of lift as to produce a constant induced angle of attack. The diameter of the circle containing the wings may be d , the cross-section of the tunnel may be circular, concentric to the wing and having the diameter D . The final two-dimensional flow is determined by its radial velocity components at the points of the inner and outer circle. The latter is at rest, hence the radial velocity at its points is zero. The inner circle moves with the velocity v , hence the radial velocity component at its points is $v \sin \varphi$, where φ denotes the angle between the radius of the point and the diameter at right angle to the motion v . Let r denote the distance of any point from the centre. Then the flow under consideration has the velocity potential

$$P = -u \sin \varphi \left(r \frac{d^2}{D^2 - d^2} + \frac{1}{4r} \frac{d^2 D^2}{D^2 - d^2} \right) \quad (1)$$

I prove this by forming the expression for the radial velocity component dP/dr

$$\frac{dP}{dr} = -u \sin \varphi \left(\frac{d^2}{D^2 - d^2} - \frac{1}{4r^2} \frac{d^2 D^2}{D^2 - d^2} \right) \quad (2)$$

Consider first the outer circle, and accordingly substitute in equation (2) $\frac{1}{2}D$ for r . This substitution gives indeed

$$\frac{dP}{dr} = 0$$

At the points of the inner circle, on the other hand, $r = \frac{1}{2}d$. This substituted in equation (2) gives

$$\frac{dP}{dr} = u \sin \varphi$$

and thus the boundary conditions for the flow are shown to be fulfilled. It complies in addition with the general, Laplace's, condition for the potential flow of a perfect fluid.

The same substitution in the expression for the potential (1) gives the potential at the points of the inner circle

$$P = -u \sin \varphi \frac{d}{2} \frac{D^2 + d^2}{D^2 - d^2} \quad (3)$$

The kinetic energy of this flow has now to be determined. Since no fluid passes through the outer circle, this is done by integrating along the inner circle alone. The kinetic energy of the flow is in general

$$\frac{\rho}{2} \int P \frac{dP}{dn} ds \quad (4)$$

the integral to be taken along all boundaries. Herein, ρ denotes the density of the fluid, P the potential, dP/dn the velocity component normal to the boundary and ds the length of an element of the boundary. In this case, the element of the boundary has the magnitude

$$ds = \frac{1}{2} d \varphi \quad (5)$$

The radial component of the velocity was $u \sin \varphi$. The potential was given in equation (3). Hence the integral assumes the form

$$\frac{\rho}{2} \int_0^{2\pi} \left(\frac{d}{2} \right)^2 \frac{D^2 + d^2}{D^2 - d^2} u^2 \sin^2 \varphi d \varphi \quad (6)$$

and the kinetic energy results to be

$$\frac{\rho}{2} d^2 \frac{\pi}{4} u^2 \frac{D^2 + d^2}{D^2 - d^2} \quad (7)$$

corresponding to the apparent additional mass of the circle

$$d^2 \frac{\pi}{4} \frac{D^2 + d^2}{D^2 - d^2}$$

or approximately

$$d^2 \frac{\pi}{4} \left(1 + \frac{2d^2}{D^2} \right)$$

The entire apparent mass of the flow, including the fluid inside the inner circle, moving with constant velocity, is therefore

$$2 d^2 \frac{\pi}{4} \left(1 + \frac{d^2}{D^2} \right)$$

Introducing now K , the area of apparent mass of the wings in an unlimited flow, that is, in this case $K = 2d^2 \frac{\pi}{4}$, and S' , the cross-section of the air current, in this case $D^2 \frac{\pi}{4}$, and expressing

d and D by means of K and S' , it results that the apparent mass of the wing is increased in the ratio

$$1 + \frac{1}{2} K/S'$$

The induced angle of attack and the induced drag are inversely proportional to this apparent mass. It follows therefore that in a tunnel with the cross-section area S' the induced angle of attack and the induced drag are decreased in the ratio

$$\frac{1}{1 + \frac{K}{2 S'}}$$

For a single wing in particular the area K is $b^2 \frac{\pi}{4}$ where b denotes the span. Hence then the induced drag and angle of attack observed in the closed wind-tunnel are smaller than the corresponding quantities would be in a tunnel of infinitely large dimensions and are decreased in the ratio

$$\frac{1}{1 + \frac{b^2}{2 D^2}}$$

I proceed now to the free jet. That flow is produced by pressures over the wings only; there is no pressure difference at the boundary of the jet. Hence the potential over the boundary, essentially identical with the impulsive pressure creating the flow, is zero. The same method as before gives almost the same flow as before, only the sign of the second term of the potential P is reversed. Hence the induced angle of attack and the induced lift are now increased in the same ratio

$$1 + K/2 S'$$

for any wing and in the ratio

$$1 + b^2/2 D^2$$

for a single wing with the span b .

PROPELLER TESTS IN CLOSED TUNNEL.

The influence of the wind-tunnel walls on the result of propeller tests has been theoretically investigated by R. M. Wood.² The results are not quite as completely and clearly brought out as Doctor Prandtl's. They seem to be disfigured by some misprints, and I am unable to bring the result as given analytically in agreement with his diagram.

Mr. Wood substitutes an ideal propeller with constant density of thrust per unit of propeller disc area and without torque for the actual propeller. I follow him herein. The air is now accelerated in direction of its original motion. Therefore the momentum is not distributed over the entire air, but remains concentrated in the air passed through the propeller disc. When passing the propeller disc it has already received half the increase of velocity. Let the velocity of flight be V and the final velocity of the slip stream be v . The velocity with which the air passes through the propeller disc is then $V + \frac{v}{2}$ (relative to the propeller) and hence the mass of air passing it per unit time is $S(V + \frac{1}{2}v)\rho$, where S denotes the propeller disc area, $D^2 \frac{\pi}{4}$ and ρ the density of air. The final increase of momentum per unit of time, equal to the thrust is $T = Sv(V + \frac{1}{2}v)\rho$. This gives a quadratic equation for v . Let C_T be

$$C_T = \frac{T}{SV^2 \frac{\rho}{2}}$$

then the equation gives

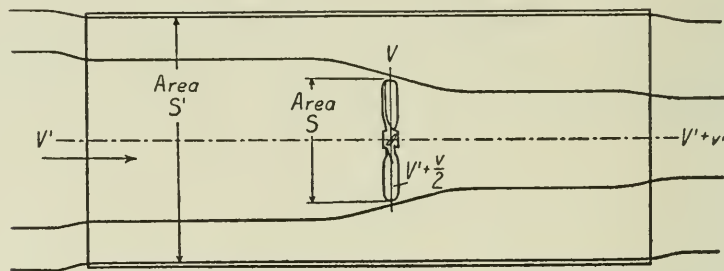
$$v/V = \sqrt{1 + C_T} - 1 \sim \frac{1}{2} C_T,$$

if C_T is very small.

In many practical cases C_T is not small enough for the use of the approximate expression. Suppose now the propeller to be surrounded by a coaxial cylindrical tube representing the tunnel as shown in Fig. 1. The length of the tube is supposed to be large, but still finite, so that in front of it and behind it the flow occupies the entire space. This tube in addition is supposed to transfer no momentum to the fluid. Its wall being parallel to the motion in all points, this is almost a matter of course. The ends, however, in this hypothetical case of a perfect fluid, even when infinitely thin, are able to transfer finite longitudinal forces since the velocity near the edges and hence the pressures may become infinite. It is supposed that these forces acting on the edges neutralize each other. This requires equal edge velocities at the entrance and at the outlet, and this again requires, approximately at least, equal velocity differences inside and outside the tube at both its ends.

The tube transferring no momentum to the fluid, the arguments used before for the propeller in the unrestricted air remain entirely unchanged. The original velocity V' in the unrestricted space, the slip stream velocity v , and velocity with which the air passes the propeller and the propeller forces are exactly the same as before. The whole configuration of the flow, however, has been changed. The original and the final velocity occur only outside of the tube and hence are farther removed from the propeller. Inside the tube these velocities cannot be found. The longer the tube is, the longer is the path at the points of which the air has already begun to change its velocity, but has not yet

FIG. 1.



Slip stream transfigured by a tube.

attained to its final velocity. This not only refers to the air passing through the propeller disc and receiving momentum, but also to the air inside the tube surrounding the slip stream. This air has a velocity inside the tube different from the original and final velocity. If the tube is long enough, the flow in front of and behind the propeller attains to steady conditions, flowing with constant velocity and pressure parallel to the axis. Neither this velocity nor that of the slip stream inside the tube agree, however, with the final velocities.

The portion of the configuration of flow outside the tube is only fictitious and does not exist with an actual wind-tunnel. The problem therefore arises to determine the original velocity V' from the observed data of the test, since this velocity V' corresponds to the velocity of flight under which the propeller is supposed to work. The area of the propeller disc S and the cross-section of the wind-tunnel S' and the thrust T are supposed to be determined. In addition the velocity of the flow must have been measured at one point at least. It is most convenient to

determine it far in front of the propeller, as there the flow is smooth and not disturbed. The velocity there may be denoted by V . In the plane of the propeller disc, outside of it, the remaining cross-section is narrow and the measurement of the velocity difficult, this the more so, as the propeller is not an ideal one and the velocity in this cross-section hardly quite constant and without fluctuations. I assume now that the change of all velocities brought about by the walls of the tunnel is small when compared with these velocities themselves. The change of the slip stream contraction is then small, too, when compared with the contraction itself. This assumption leads to results exact enough for the practical application. In addition this proceeding can be considered as the first step to a more exact computation. From this assumption, it follows that the air inside the tunnel, *not* passing through the propeller disc, flows through the cross-sections

$$(a) \text{ far in front of the propeller : } S' - S \left(1 + \frac{v}{2V} \right)$$

$$(b) \text{ in the plane of the propeller : } S' - S$$

$$(c) \text{ far behind the propeller : } S' - S \left(1 - \frac{v}{2V} \right)$$

Its average velocity (b) in the propeller plane being denoted by W , the velocity in front of and behind the propeller would result

$$W_{(a)} = W_{(b)} \frac{S' - S}{S' - S \left(1 + \frac{v}{2V} \right)}; \quad W_{(c)} = W_{(b)} \frac{S' - S}{S' - S \left(1 - \frac{v}{2V} \right)}$$

Outside the tube the velocity is V' . But as demonstrated before, the velocity difference inside and outside the tube is equal at both ends. This gives the condition

$$W_{(b)} = V'$$

since $\frac{v}{2V}$ is a small quantity and it appears the simple result :

The average velocity in the propeller plane outside the propeller disc agrees with the fictitious velocity of flight.

The problem would thus be solved in the simplest way. But as mentioned before, it is not always practical to measure the velocity very near to the propeller. It remains therefore to find a simple relation between the fictitious velocity of flight V' and the velocity V far in front of the propeller. That is now easy

enough. The velocities V and V' are inverse as their cross-sections $S' - S \left(1 + \frac{v}{2V}\right)$ and $S' - S$, hence

$$V' = V \frac{S' - S}{S' - S \left(1 + \frac{v}{2V}\right)} \sim V \left(1 + \frac{v}{2V} \frac{S}{S' - S}\right) \sim V \left(1 + \frac{v}{2V} \frac{S}{S'}\right)$$

or the magnitude of v substituted

$$V' \sim V \left(1 + \frac{1}{2} (\sqrt{1 + C_T} - 1) \frac{S}{S'}\right)$$

That is the formula which I wished to obtain. For very small values of C_T it becomes

$$V' \sim V \left(1 + \frac{C_T}{4} \frac{S}{S'}\right)$$

but in practice C_T is often not small enough for the application of this simplified formula.

Mr. Wood obtains the final approximate formula

$$1 - \frac{V'}{V} = 55 X^2 \frac{T}{\rho a_3 V^2}$$

where a_3 denotes the cross-section of the slip stream and X its ratio to the cross-section of the wind-tunnel. If we assume two misprints and write instead of this formula

$$1 - \frac{V'}{V} = .55 X \frac{T}{\rho a_3 V^2}$$

Mr. Wood's formula almost agrees with the one obtained by myself for small thrust coefficient C_T .

PROPELLER TESTS IN A FREE JET.

With propeller tests in a free jet no correction of the velocity is necessary. The surface of the jet is a surface of constant pressure, hence the cylindrical parts of the flow far in front and far behind the propeller have the same pressure. Therefore the arguments used for the propeller in unrestricted air remain quite unchanged. The velocity far in front of the propeller is directly identical with the fictitious velocity of flight. The contraction of the slip stream remains unchanged too. The exact shape of the slip stream is slightly changed, but this has no noticeable effect on the air forces in general.

WIND-MILL TESTS.

The arguments used for propellers are good for wind mills, too. Wind-mill tests in a free jet are in no need for a correction. The fictitious velocity of flight for wind-mill tests in a closed tunnel with the velocity V far in front of the wind mill is

$$V' = V \left(1 + \frac{v}{2V} \frac{S}{S'} \right)$$

as before.

With wind mills v/V is negative and has the value

$$\frac{v}{V} = 1 - \sqrt{1 + C_T}$$

Hence

$$V' = V \left(1 - \frac{S}{2S'} (\sqrt{1 + C_T} - 1) \right)$$

or approximately for small thrust coefficient C_T .

$$V' = V \left(1 - \frac{C_T}{4} \frac{S}{S'} \right)$$

CONCLUSION.

The investigation thus finished showed that the open jet decreases the angle of attack of a wing and hence its lift, increasing the drag. It has no noticeable effect on the results of the other tests mentioned, unless the models are exceedingly large. The closed tunnel increases the angle of attack of a wing, thus increasing its lift and decreasing its drag. The velocity measured far in front of the model is too large with propeller tests and too small with wind-mill tests. Formulas giving the necessary corrections are given in each single section.

REFERENCES.

- ¹ L. Prandtl: "Applications of Modern Hydrodynamics to Aeronautics," Sec. F., N.A.C.A., Report No. 116.
- ² R. M. Wood: "Some Notes on the Theory of an Air Screw Working in a Wind Channel," British A. C. A., R. and M., No. 662.

A Theory of Meteors and the Density and Temperature of the Outer Air to Which it Leads. F. A. LINDEMANN and G. M. B. DOBSON, University of Oxford. (*Proc. Roy. Soc.*, A 717.)—"A meteor is an extra-terrestrial particle which enters the air at high speed, it becomes visible (owing to collision of the fast vapour molecules with air molecules) when its surface becomes hot enough to

evaporate appreciably, and it disappears when it has evaporated practically completely." "All meteors move at a speed great compared to the velocity of sound." The meteor strikes the earth's atmospheric envelope and upon reaching air of a certain density it forms in front of it a cap of condensed air, heated adiabatically by the compression. There is an influx of heat from this cap to the material of the meteor whose temperature rises until vapor is given off.

The authors show that it is possible to give equations connecting the various quantities concerned in the result and that these equations are not so replete in inaccessible quantities that no definite deductions can be drawn. On the contrary quite definite and astonishing conclusions are reached when the equations are applied to the observed data of meteors. "The heights, paths and velocities of some thousands of meteors have been observed. They appear, in general, at heights between $1.6 \cdot 10^7$ and $7 \cdot 10^6$ cm., and disappear at heights below $1.2 \cdot 10^7$ cm., mostly at about $8 \cdot 10^6$, though some, of course (the so-called meteorites) reach the ground. Velocities from $9.5 \cdot 10^5$ to $1.6 \cdot 10^7$ cm./sec. have been recorded."

The mass of a meteor can be computed from the equations. A meteor traversing a distance of $6 \cdot 10^6$ cm. in 1.5 seconds, "and appearing at a distance of $1.5 \cdot 10^7$ cm. as bright as a first-magnitude star" will have a mass of $6.25 \cdot 10^{-3}$ gram. If it is made of iron, its diameter is one-ninth cm.

The most surprising deductions are those relating to the temperature and density of the air at high altitudes. "Some thirty years ago Teisserenc de Bort announced the discovery that the temperature gradient in the atmosphere, which amounts to some $6.5 \cdot 10^{-5}$ degree/cm. for the first 10 km., becomes negligibly small at greater heights. Since this time it has become usual to treat the temperature as constant for all heights above this limit, and various detailed numerical estimates, extending to heights of hundreds of kilometres, have been published, which are based on this assumption. So far, however, no evidence for it has been adduced beyond the 'ballon sonde' observations, which scarcely extend above 25 km." It is shown "that existing observations enable us to say with considerable certainty that the density at heights above 65 km. is very much higher than is commonly supposed, and that the temperature must increase from its value of something like 220° abs. at heights between 12 and 50 km. to something like 300° abs. at those heights." This difference of density is no small matter for at 150 km. it is calculated to be 1000 times as great as it has been believed to be. The higher temperature at great heights is explained by the importance of ozone in the outer portions of the atmosphere. These new results will need to be regarded in forming theories of the aurora, for at the lower limit of this the density now comes out 100 times as great as it was held to be.

G. F. S.

AN IMPULSE ELECTRIC MOTOR FOR DRIVING RECORDING INSTRUMENTS.*

BY

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SUMMARY.

THE chief purpose in undertaking the development of this synchronous motor was the creation of a very small, compact power source, capable of driving the film drums of the recording aircraft instruments designed by the staff of the National Advisory Committee for Aeronautics.

The working parts of the motor are few and simple. They consist of four spool type field coils, a reciprocating armature, a ratchet wheel and two pawls. The field coils, operating in pairs, alternately pull the armature from one pair of pole faces to the other pair. This reciprocating motion is transmitted to the ratchet wheel through the two pawls, motion in either direction producing a positive advance of the wheel. Rotation of a very regular character is thus secured.

The motor is $1\frac{3}{8}$ inches long, $1\frac{3}{16}$ inches wide and $\frac{7}{8}$ inch high, with a volume of 1.43 cubic inches, and a weight of .165 pound (75 gms.). It produces approximately 6.0×10^{-5} H.P., with an efficiency of 1.0 per cent. The speed range is from 0 to 35 R.P.M., the torque being .234 pound-inch (269.6 g.-cm.) at the lower speeds with 8 volts applied.

Due to its small size and light weight, its inherent slow speed and property of absolute synchronization, the motor is particularly well adapted to aircraft instrument work. Application of this type of power source may also be made to automatic recording instruments of all kinds, to indicating devices requiring absolute precision of movement, and to remote control work.

* Communicated by Dr. Joseph S. Ames, Director, Office of Aeronautical Intelligence, National Advisory Committee for Aeronautics and Associate Editor of this JOURNAL.

INTRODUCTION.

The specific problem which was responsible for the development of this direct current synchronous motor, was that of driving the film drum of an instrument called the sun kymograph.

The requirements of this instrument are four-fold: First, the drive must be slow speed; second, the rotation must be uniform and regular; third, the part of the drive attached to the instrument must be small, compact and light in weight; and fourth, the connecting link between the instrument and airplane must be flexible.

To meet these requirements three forms of mechanical drives, and two types of small electric motors were investigated and tried.

METHODS AND APPARATUS.

The mechanical drives investigated consisted of flexible cables which received their power from a constant speed motor mounted on the floor of the airplane. These cables drove the kymograph film drum through a small clutch attached to the instrument.

The three forms consisted, first, of a solid wire enclosed in a flexible housing; second, of a standard Van Sicklen tachometer cable and housing, and third, of a double opposed spring cable (Van Sicklen), without a housing, but guided at intervals by rings.

The results obtained with these drives were unsatisfactory. Due to the slow speed required, which caused a spasmodic sticking and releasing of the cable within its housing or guiding rings, all three types imparted a very irregular rotation to the film drum. The flexibility of these drives was also inadequate for the work involved.

The first type of electric drive investigated was a low-frequency alternating-current motor. This was built very much like a standard direct-current telephone relay. It depended for its action on the cyclic attraction of a small laminated bar armature to and from a pair of spool type coil magnets. A spring pawl transmitted the reciprocating motion of the armature to a ratchet wheel.

A second form of alternating current motor, similar in construction and principle to the polarized relay or the alternating current bell ringer, was also investigated. As in the first form of this type of motor, a pawl transmitted the oscillating motion of the armature to a ratchet wheel.

Both of these motors operated fairly well with very light loads. But a load equal to that of a film drum retarded the armature sufficiently to destroy the synchronism between armature and magnetic flux.

In the second form of motor, it was particularly noticed that the frequency of the alternating current had to coincide exactly with the natural period of the oscillating parts for the motor to function. Also the starting torque of the motor was very low, and the efficiency of both motors was less than one-twenty-fifth of one per cent. Hence these two electric drives were also inadequate and unsatisfactory.

The second and successful type of electric drive investigated was built much like a standard telephone relay, but had double opposed electromagnets. These alternately pulled the armature from one pair of pole faces to the other. This reciprocating motion was transmitted to the ratchet wheel through a pawl, power being directly imparted in only one direction.

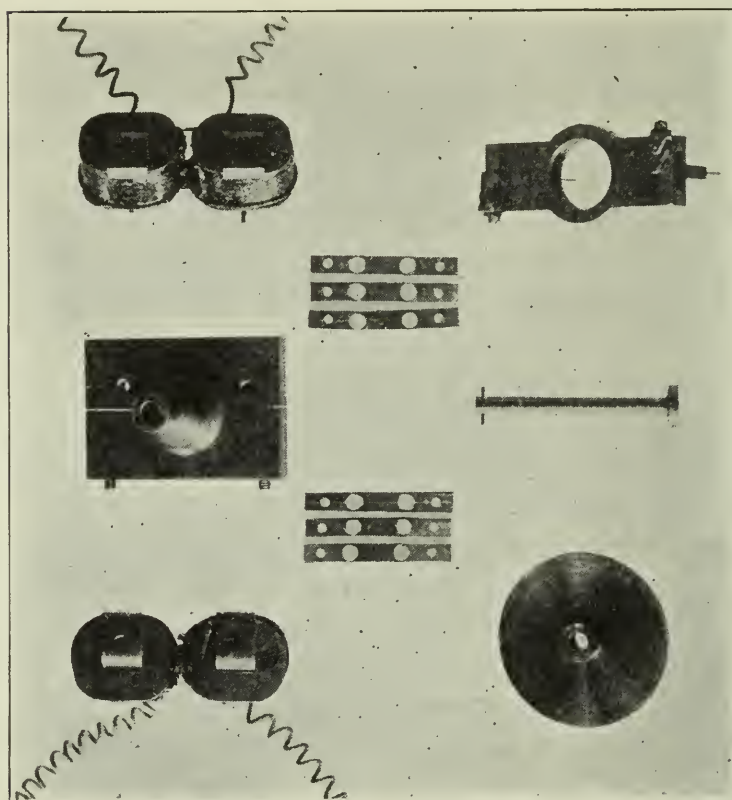
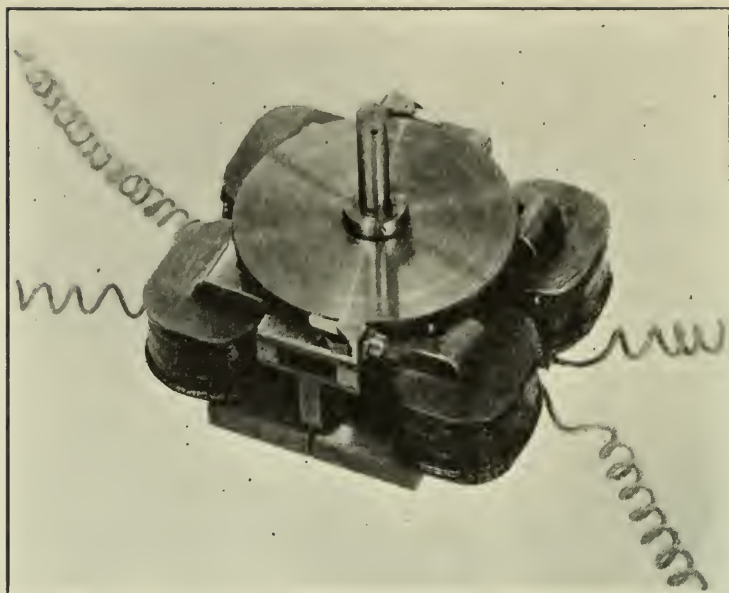
This form of motor gave a somewhat intermittent rotation, there being sixty separate impulses for one revolution of the ratchet wheel.

The final form of the motor, however, utilizes the motion of the armature in either direction to give a positive advance to the wheel. This was accomplished by two pawls acting on opposite sides of the ratchet wheel as shown in Figs. 1 and 2. The rotation secured in this manner is very regular, there being 480 continuous and connected power strokes for one revolution of the wheel.

Since it may not be fully apparent, from the foregoing brief description, how a reciprocating armature can impart definite unidirectional power strokes to a ratchet wheel a detailed description of the operation follows.

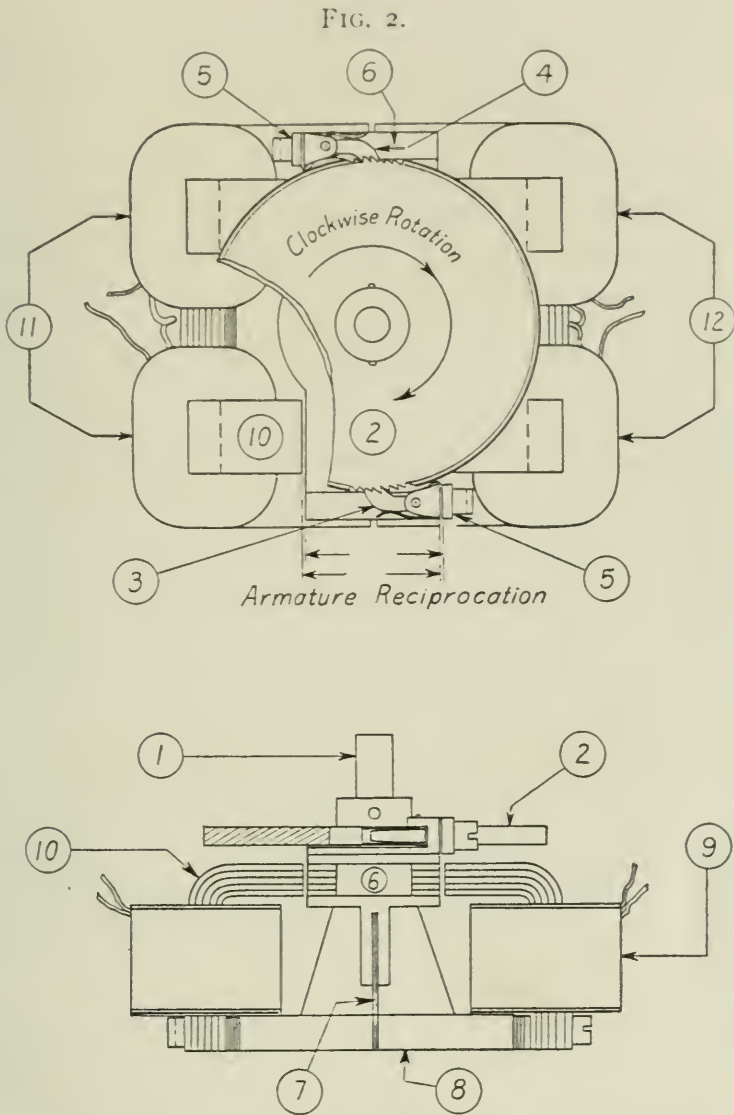
Referring to Fig. 2, it will be seen that the ratchet wheel rotates about a vertical axis passing through the centre of the motor; also that it lies above the field poles and reciprocating armature, and between the two pawls, which latter are mounted in brackets at either end of the armature. The armature is supported by two leaf springs fixed in the base and is returned by these springs from either pair of pole faces to a neutral position half-way between them.

FIG. 1.



Direct current synchronous motor and parts.

The moving parts of the motor consist of the armature, the two pawls and the ratchet wheel. There are no connecting rods or bell cranks.



Diagrammatic drawing of direct current synchronous motor.

1, vertical shaft; 2, ratchet wheel; 3, pawl A; 4, pawl B; 5, pawl brackets; 6, armature; 7, armature springs; 8, base; 9, field coils; 10, field poles; 11, left electromagnet; 12, right electromagnet.

Assuming now the left electromagnet to be energized, the action from the neutral position is as follows:

The armature is pulled to the left until it reaches the pole faces of the left electromagnet. During this motion, pawl A has rotated the wheel clockwise one-quarter of a tooth. At the same time pawl B has ratcheted back in a counter-clockwise direction

one-quarter of a tooth and has dropped into position behind the tooth over which it has just moved. The armature is now in position for a complete power stroke from left to right.

Assuming the left electromagnet to be de-energized, the armature springs start to return the armature to the neutral position. This action does not rotate the wheel under load but serves only to take up the slight play between pawl *B* and the three teeth of the wheel on which it is now exerting some pressure.

Approximately one-sixtieth of a second elapses during the above action, after which the right electromagnet is energized.

The armature is now pulled to the right until it reaches the pole faces of the right electromagnet. During this motion pawl *B* rotates the wheel clockwise, as before, one-half a tooth. At the same time pawl *A* is ratcheted counter-clockwise also a half tooth. Since the wheel has been rotated clockwise a half tooth and pawl *A* moved counter-clockwise a half tooth, it will be seen that the relative motion between the two is equal to a whole tooth.

Therefore, pawl *A* drops into position behind the tooth over which it has just moved. Thus the power stroke has been completed and the armature brought into position for the following stroke from right to left.

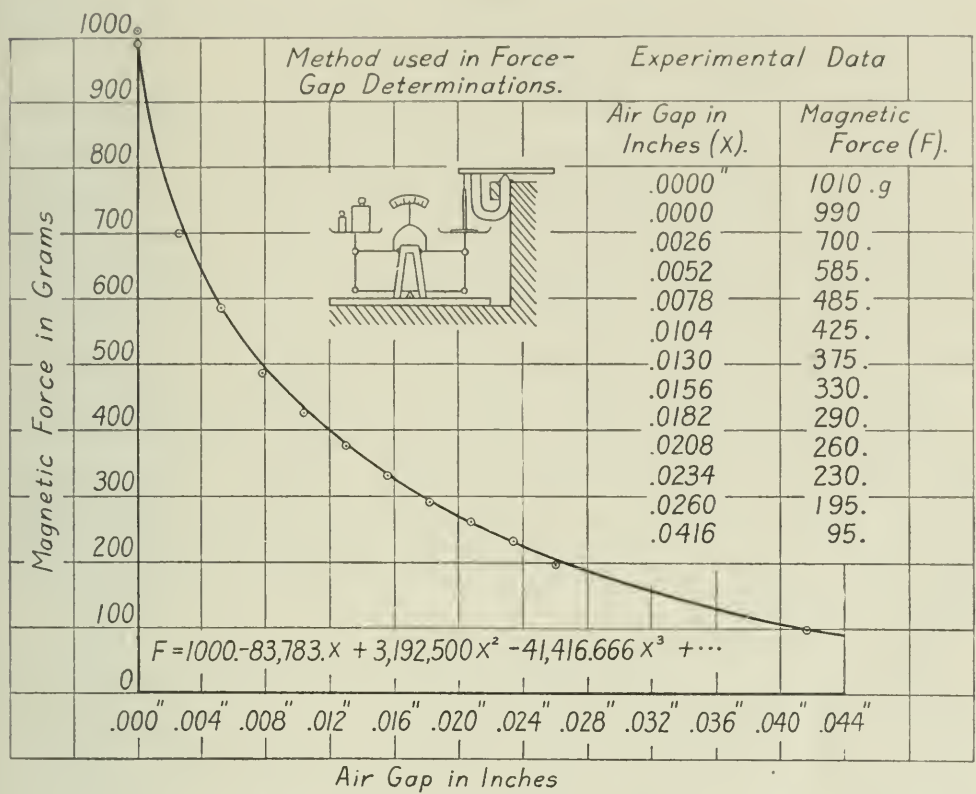
The sequence of operations from right to left are exactly the same as those from left to right with the one exception that pawl *A* now rotates the wheel, while pawl *B* ratchets into position over another tooth. Hence the power strokes proceed from right to left and from left to right, the wheel always being rotated clockwise.

Since it requires two strokes of the armature to move the wheel one tooth, and since the wheel has 240 teeth, it requires 480 power strokes to rotate the wheel one complete revolution. Hence the inherent slow speed of the motor.

The maximum air gap required in this motor between the armature and either pair of pole faces is very small, actually about .008 inch. This gap varies in operation from .008 inch to zero, so that the average gap is only .004 inch. Hence the efficiency of the magnetic circuit is high. This is accomplished by using ratchet teeth of small pitch, and by the fact that a complete power stroke requires an air gap of only one-half the tooth pitch.

Referring to Fig. 3 it will be seen that the magnetic pull between two plane surfaces which are separated by small air gaps is neither inversely proportional to the gap nor to the square of the gap, but follows a law of the following form: $F = C - C_1X + C_2X^2 - C_3X^3 + \dots$. In this equation F is the magnetic force or pull; C , C_1 , C_2 and C_3 are constants determined by the size and shape

FIG. 3.



Magnetic force variation for small air gaps.

of the poles faces and by the total magnetic flux; and X is the gap between magnet and armature.

It was found that the magnetic pull in this motor at zero gap was 1150 grams (2.54 lbs.) and at .008 inch gap, 550 grams (1.21 lbs.). The armature springs therefore were designed to equalize this varying magnetic force so as to give a pull of 850 grams (1.87 lbs.) throughout the whole power stroke. Thus the springs store 3.05 cm.-g. (.00264 in.-lb.) of energy during the last half of each power stroke and return it during the first half of the following power stroke.

The alternate energizing and de-energizing of the left and

right electromagnets is accomplished by a distributor driven by a constant speed motor in an average case at about 720 R.P.M. This distributor makes and breaks the electric circuit for each electromagnet of the motor once for each revolution. Hence at 720 R.P.M. of the distributor the motor armature has transmitted 1440 power strokes to the ratchet wheel, thus producing a motor speed of three revolutions per minute. This speed is readily controlled so that a range of from zero to 16,800 power strokes per minute may be realized. This gives a motor speed range of from zero to 35 R.P.M.

By the use of this method of commutation, and speed control, it will be seen that absolute synchronism between any number of motors is readily obtained by merely taking their current supply from the same distributor. Thus any number of instruments may not only be operated in absolute synchronism with each other, but, if the distributor be chronometrically controlled, absolute speed regulation and timing may also be realized.

The performance of the motor in a complete laboratory test proved entirely satisfactory. This test was conducted to determine, first, the complete speed range; second, the maximum torques; third, the effect of varying the distributor-commutator time-contact ratios; and fourth, the current consumed under the different conditions.

The time-contact ratio, as here used, means the ratio of the time the motor is cut in circuit to the time the motor is cut out of circuit. The time-contact ratio is taken over two complete power strokes or one revolution of the distributor-commutator. This is also called a cycle and the amount of actual contact is determined by the number of degrees of commutation per cycle.

It will be readily understood that to obtain the best efficiency from the motor, the current supplied through the distributor-commutator should be cut out the instant the armature has completed its power stroke. In order to accomplish this result, without any complication, the correct length of the distributor-commutator segment, which makes and breaks the circuit and thus produces a power stroke, was determined in this test for all speeds and torques.

The data obtained are tabulated in Table I. Curves showing the torques in gram-centimetres, speeds, degrees of commutation, efficiencies, current consumed in amperes, horsepower and the

TABLE I.
Direct Current Synchronous Motor Performance Data.

Torque in G.-Cm.	Degrees of Commutation per Cycle.											
	45°		90°		135°		180°		225°		270°	
	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.	P. S.	Amp.
265.	0	.131	0	.263	0	.394	0	.523	0	.656	0	.788
232.6	5,400	.67
200.5	1,600	.130	3,200	.24	4,200	.33	5,100	.41	6,000	.49	8,920	.53
174.6	1,800	.115	4,100	.22	5,140	.30	6,400	.38	7,920	.45
135.8	2,400	.11	4,900	.19	6,600	.27	8,000	.33	8,800	.41	10,800	.49
103.5	2,900	.10	5,700	.175	7,800	.24	9,300	.31	11,000	.34	12,000	.42
84.1	3,060	.09	6,300	.17	8,700	.23	11,000	.29
64.7	3,500	.08	7,400	.155	9,600	.20	12,400	.25	12,400	.32	13,800	.39
45.25	8,400	.15	10,780	.18
32.16	4,800	.075
0.00	7,000	.06	12,400	.10	14,000	.16	15,100	.19	16,200	.23	16,800	.29
											17,000	.36

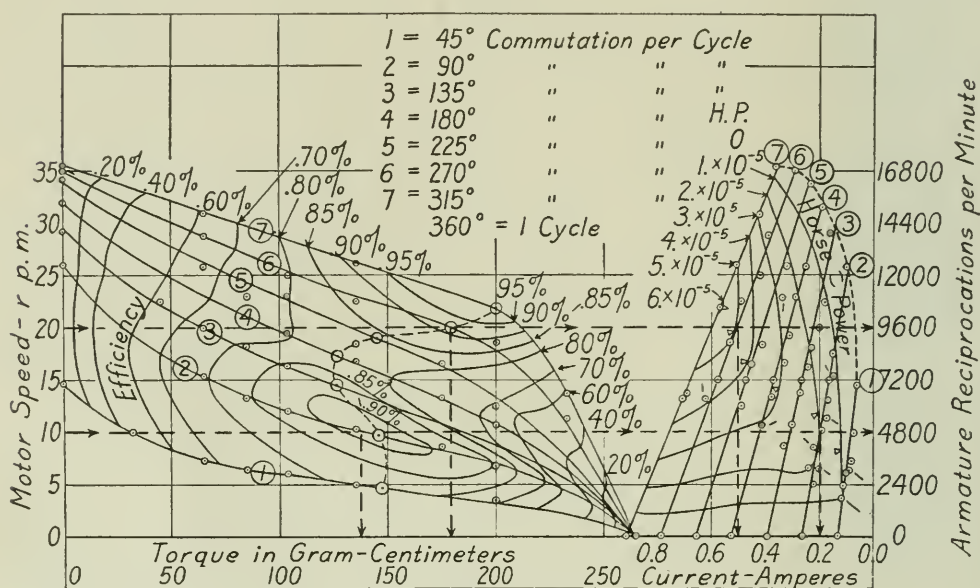
P. S.=Power strokes per minute.
Amp.=Current consumed at 8 volts.

number of armature reciprocations per minute are plotted on curve sheet Fig. 4.

Thus, following the dotted lines, starting at 10 or 20 R.P.M., we may find the other characteristics of the motor for any specific number of degrees of commutation per cycle.

R.P.M.	10	20
Degrees of commutation per cycle	90°	270°
Torque	138	179
Efficiency	0.91%	0.92%
Current amperes	0.20	0.50
Horsepower	1.8×10^{-5}	4.9×10^{-5}
Armature reciprocations per minute.....	4800	9600

FIG. 4.



Performance chart of type "B" direct current synchronous motor.

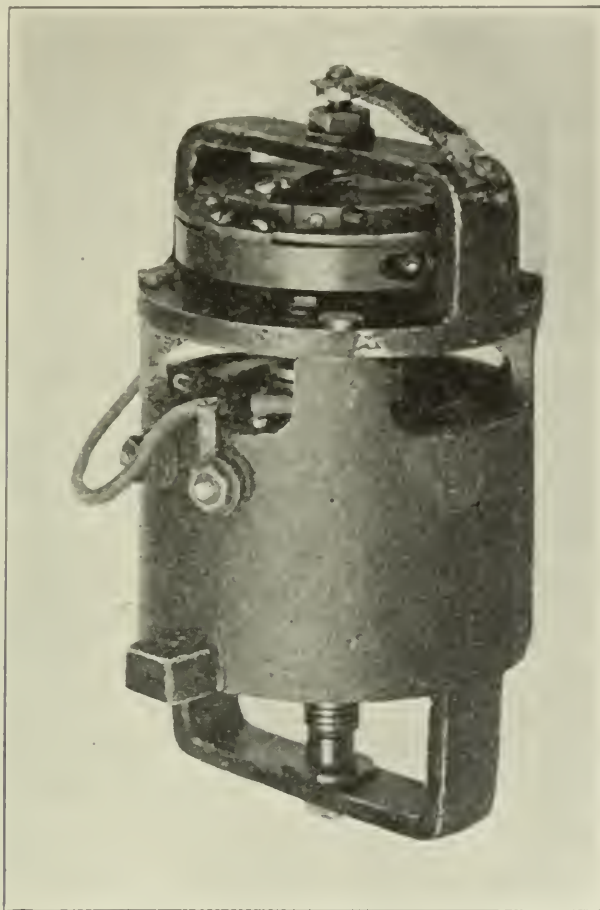
RESULTS.

The new type of power source for aircraft instruments has the following specifications:

- (1) Size: Length, $1\frac{3}{8}$ " (3.49 cm.); width, $1\frac{3}{16}$ " (3.02 cm.); height, $\frac{7}{8}$ " (2.22 cm.).
- (2) Weight: 75 gms.
- (3) Speed range: 0 to 35 R.P.M.
- (4) Current consumption: 0.1 to 0.9 amperes at 8 volts.
- (5) Torque (max.): 269.6 g.-cm.
- (6) Power (max.): 6×10^{-5} H.P.
- (7) Efficiency (max.): .99 per cent.

As it may be interesting to compare the impulse motor with the D.C. governed series motor (Fig. 5) now used in the instruments of the committee, the following table is attached:

FIG. 5.



D.C. governed series motor.

Size: 2.5" (6.35 cm.) \times 2.5" (6.35 cm.) \times 4.2" (10.67 cm.).

Weight: 750 gms.

Speed range: 500-2500 R.P.M.

Current consumption: Normal, 1.75 amps. at 8 volts.

Current consumption: Starting, 10.5 amps. at 8 volts.

Power (max.) at 1080 R.P.M. = .0051 H.P.

Power (max.) at 1790 R.P.M. = .0054 H.P.

Efficiency at 1080 R.P.M. = 12.7 per cent.

Efficiency at 1790 R.P.M. = 18.8 per cent.

Torque required to turn standard film drum with no reduction gearing varies from 27 g.-cm. to 270 g.-cm.

Efficiency of combined system of this type of motor and gearing when driving a good drum = .007 per cent.

The advantages of the impulse type of motor for instrument work are:

(1) Size and shape permit easy installation in the instrument base, thus providing space for additional apparatus, or making possible a material reduction in the size of the instrument. Its volume is 1.43 cubic inches.

(2) Light weight.

(3) Inherent low speed.

(4) Low current consumption, thus decreasing the number of storage batteries necessary for average flight work to approximately 40 per cent. of the present requirement.

(5) Constant torque at the speed range used.

(6) High efficiency for its size.

(7) Absolute synchronism or zero speed variation between any number of like motors.

(8) Normal speed instantaneously on closing the switch.

(9) Dead stop instantaneously on opening the switch.

(10) Remote control of speed of all motors in operation from the distributing source.

(11) Long life due to low-bearing pressures. (1) Pawl-bearing pressure 300 lbs./sq. in. (2) Main-bearing pressure 12 lbs./sq. in.

(12) Low construction cost due to: (1) Few parts; (2) spool type coils; (3) elimination of rotating contacts and brushes.

Italy Searching for Oil.—The “Drang nach Osten” was originally a pressure for many commercial advantages, but of late the main object of the great nations in securing opportunities in the East is to control the oil-fields. Great activity is now evident in the exploration of all regions that may yield this liquid, which has become important in peace and war. From a recent issue of the *Bollet. Chimico-Farmaceutico* (1923, lxii, 195) it is learned that Italian authorities are aroused to the necessity of securing oil-fields and have begun experimental borings within their own territory. A committee of geologists has been appointed to conduct the investigations. Some small sources of oil already exist. Apparatus for deep borings was obtained from Germany through the reparations agreement. One boring made in 1921 reached a depth of 479 metres (about 1600 feet) from which a yield of about 200 gallons per day has been obtained. In other regions surface indications of oil and of gas have been detected. A school for instruction in oil exploration has been organized. H. L.

MOTION PICTURE PHOTOGRAPHY FOR THE AMATEUR.*

BY

C. E. K. MEES, D.Sc.

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Associate Editor, Member of the Institute.

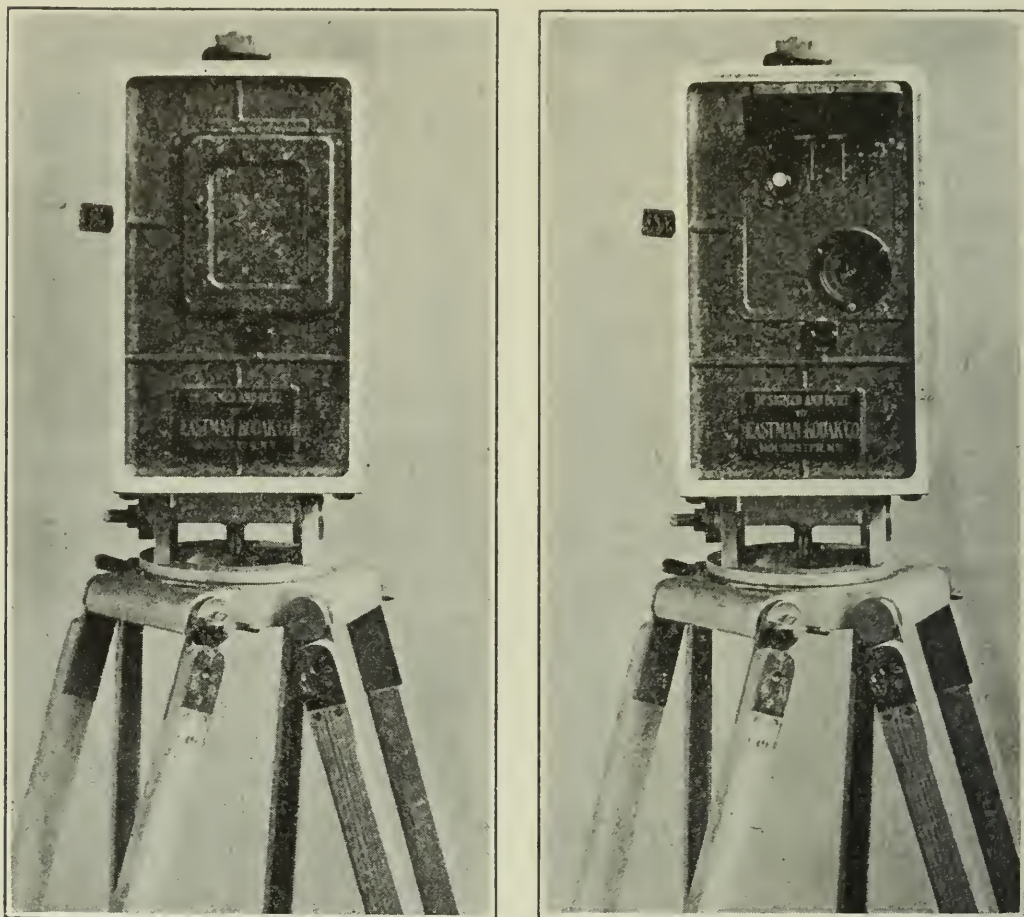
AMATEURS have played a great part in the development of photography. The early workers in photography were naturally amateurs, though the first successful process, that of Daguerre, was utilized chiefly for making portraits and was the process first used by professional photographers. While Daguerre's process was being exploited, however, Fox Talbot discovered his process in which a negative was made and then printed, the practice followed at the present time, and in which the exposure, insufficient to produce a visible image, was followed by development to obtain a negative of sufficient strength for printing. Talbot, in fact, laid the foundations for our modern systems of photography. Scott Archer, the inventor of the wet collodion process, which followed the calotype process of Fox Talbot, and Doctor Maddox, who made the first gelatin emulsion, were both amateurs, and all the early work on dry plates was done by amateurs until about 1880, when the manufacture of dry plates on a commercial scale was fully established.

Important as was the work of amateurs, however, the possibilities of amateur photography were necessarily limited by the very cumbersome equipment which was required for the wet plate process, and even when dry plates became available, the portability of apparatus and the simplicity of photography were very far from their present level. Marked as has been the improvement in apparatus for the utilization of dry plates, the greatest step in the making of photography available to everybody was the development of the film camera by George Eastman.

* Presented at a meeting of the Sections of Physics and Chemistry and Photography and Microscopy of The Franklin Institute held Thursday, February 1, 1923, and published as Communication No. 170 of the Research Laboratory of the Eastman Kodak Company.

The causes that restricted the use of photography by amateurs before the coming of the kodak have operated to limit the use of motion picture photography by other than professional photographers. The apparatus required is very heavy and cumbersome; the standard motion picture camera, tripod, and magazine form a heavy load for one man, and in addition the cost of the film is

FIG. 1.



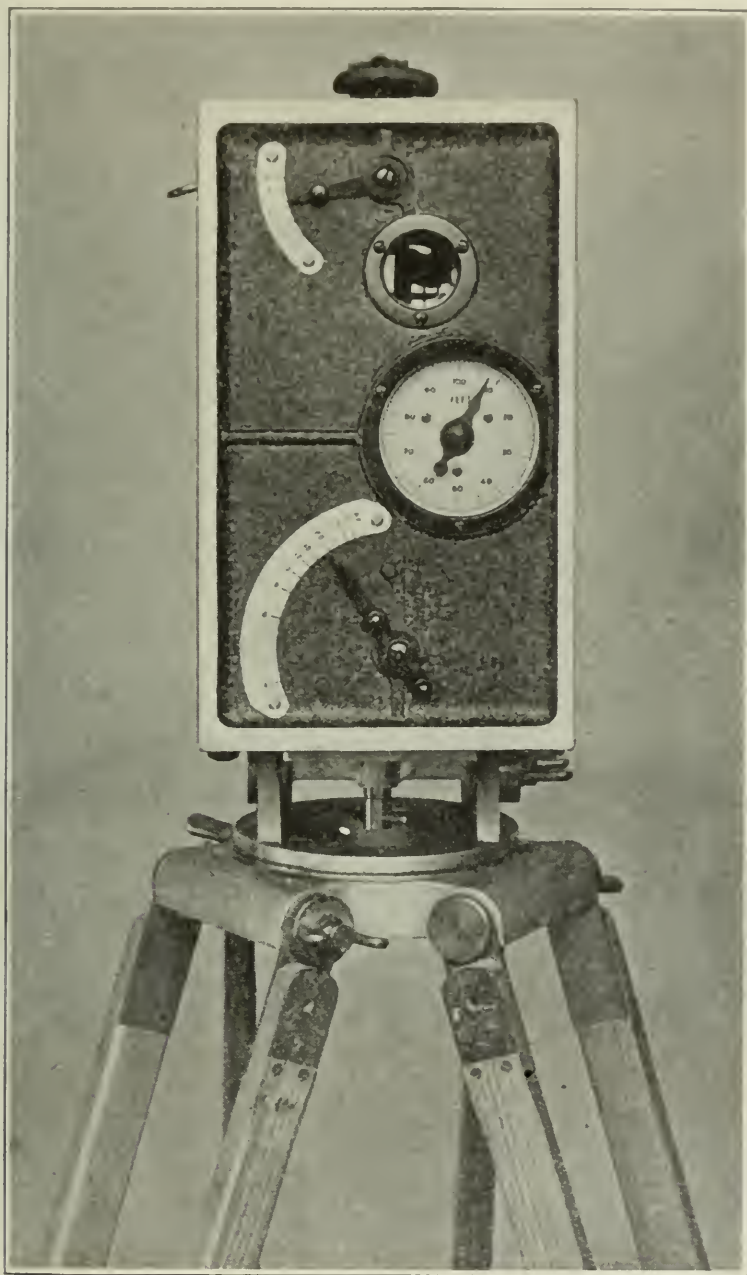
Front of the Cine Kodak.

very great. The cost of making a negative and projecting the picture upon the screen is approximately fifteen cents for each foot of film, which in projection lasts one second on the screen.

Motion pictures are obtained by making a series of photographs of the object upon a long strip of film, each picture being a representation of the object at one particular moment. Sixteen of these pictures are taken every second, and when they are

projected upon the screen, the different phases of movement blend together and give the appearance of motion. The film is held

FIG. 2.

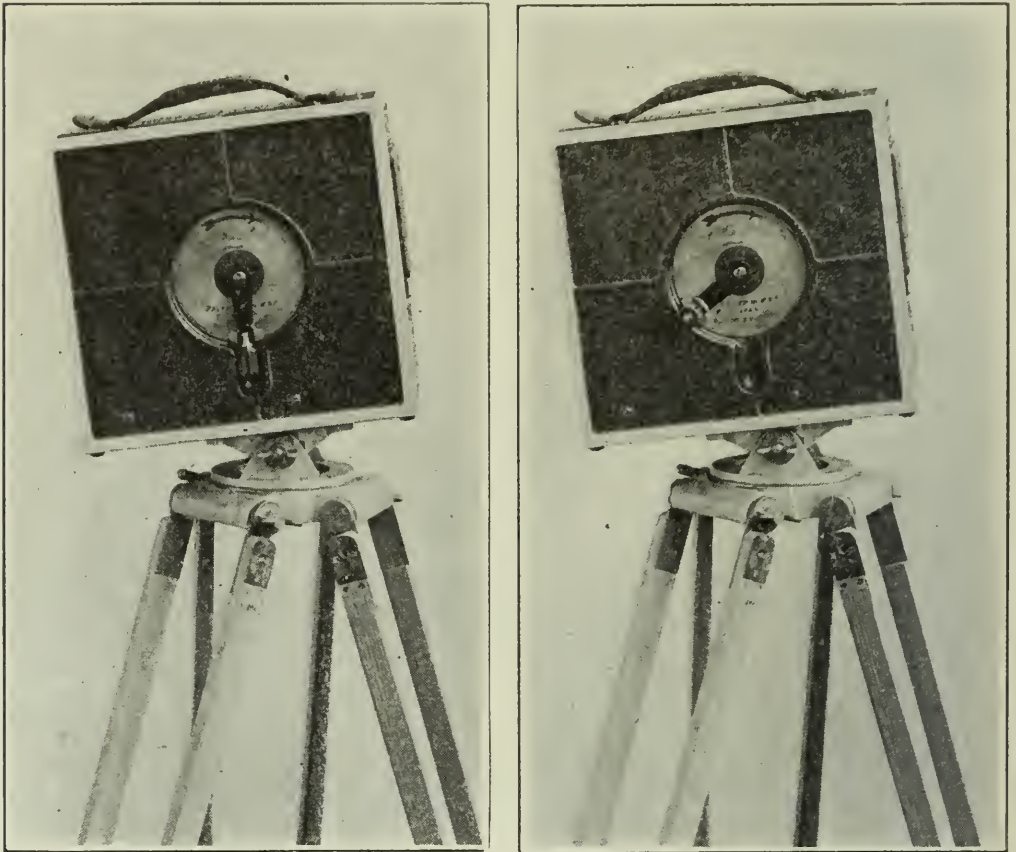


Back of the Cine Kodak.

stationary while the picture is taken or projected and then is moved forward very quickly to a new position and is held still again, so that sixteen times a second the film is moved forward,

and sixteen times a second it must be stopped. This movement is accomplished by what is called the "intermittent" mechanism in the camera or projector, the film being pulled down by claws which catch in the perforations, pull it down into its new position by the height of one picture, and then come out of the perforations again, leaving the film motionless until, as the movement

FIG. 3.



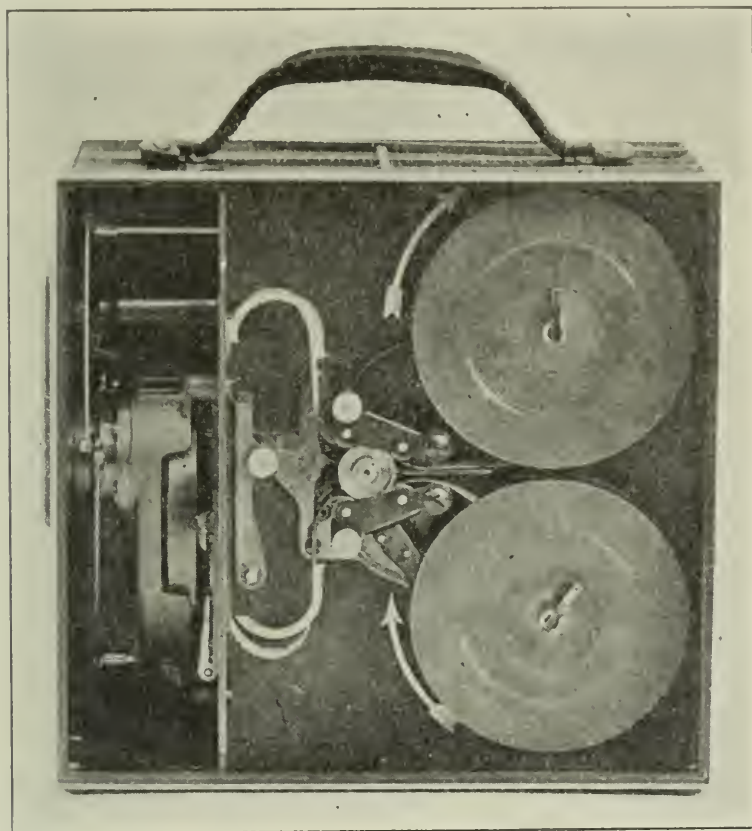
Crank side of the Cine Kodak.

of the mechanism continues, they re-engage and pull the film down again. In projectors, a sprocket with teeth on it instead of claws, which engage in the perforations, is sometimes moved intermittently to pull the film down.

The whole system of amateur motion picture photography which has been worked out by the Eastman Kodak Company is founded on film smaller than that used in the standard camera and on a new process used in finishing it, but of almost equal importance is the design of the apparatus in which the film is used.

The camera was designed and built in the instrument shop of our optical factory and is, on the whole, of standard type. It resembles, in fact, a standard motion picture camera of the highest grade, but in amateur size. No attempt has been made to cheapen the camera by the omission of any necessary feature or by any undue simplification. Our object was to produce an instru-

FIG. 4.



Mechanism with the door removed—with film.

ment which would take pictures equal in every respect to those which the professional could obtain. The lens is a kodak anastigmat working at $f/3.5$, which enables photographs to be taken under the worst conditions of light. The finder is just above the lens (Fig. 1) and by an ingenious attachment changes the position of its image as the lens is focused, thus always showing the image in the correct position. The lens has a focusing lever carried through to the back which can be focused for any distance from infinity to four feet. The diaphragm control is in the left-

hand corner and can thus be read easily. In the centre of the back is the footage indicator which shows the number of feet of film which have been used (Fig. 2). The crank is put out of the way into a recess when not required (Fig. 3). It is turned normally twice a second, taking pictures at the standard rate of sixteen pictures a second. The mechanism is of the standard motion picture type (Fig. 4), the film being pulled down by means of a claw operated by a cam mechanism.

In order to load the camera, the film spool (Fig. 5) has its outer cover removed and is then placed on the upper spindle pro-

FIG. 5.

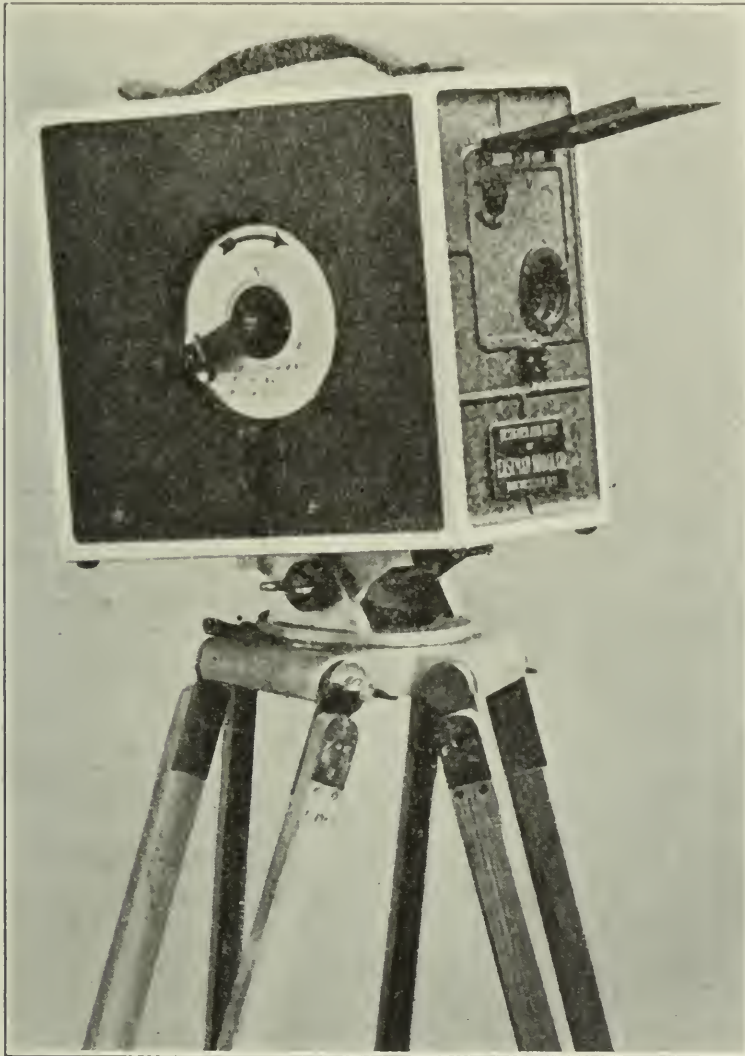


Film spool.

vided for it. To the film there is attached a paper leader of the same width as the film and perforated in the same way. Two feet of this are pulled out and are threaded over the sprocket of the camera on to which it is held by a presser plate, down through the gate, where the claws engage in the perforation, a loop being formed above the gate, as is indicated on the camera mechanism, through another loop, which is also indicated, back under the sprocket, and thence to the bottom spool, in which the end of the paper is inserted, and a few turns made to ensure everything being right. The inner cover is then removed from the spool, the film being protected for a few seconds only by the paper leader. The door is placed on the camera, and the four remaining feet of paper leader are run off. The footage indicator

at the back of the camera is then set at zero, and the camera is loaded ready for use with 100 feet of film. After all the film has been exposed, cranking is continued for five more feet, thus winding up another paper leader on to the exposed film. The

FIG. 6.



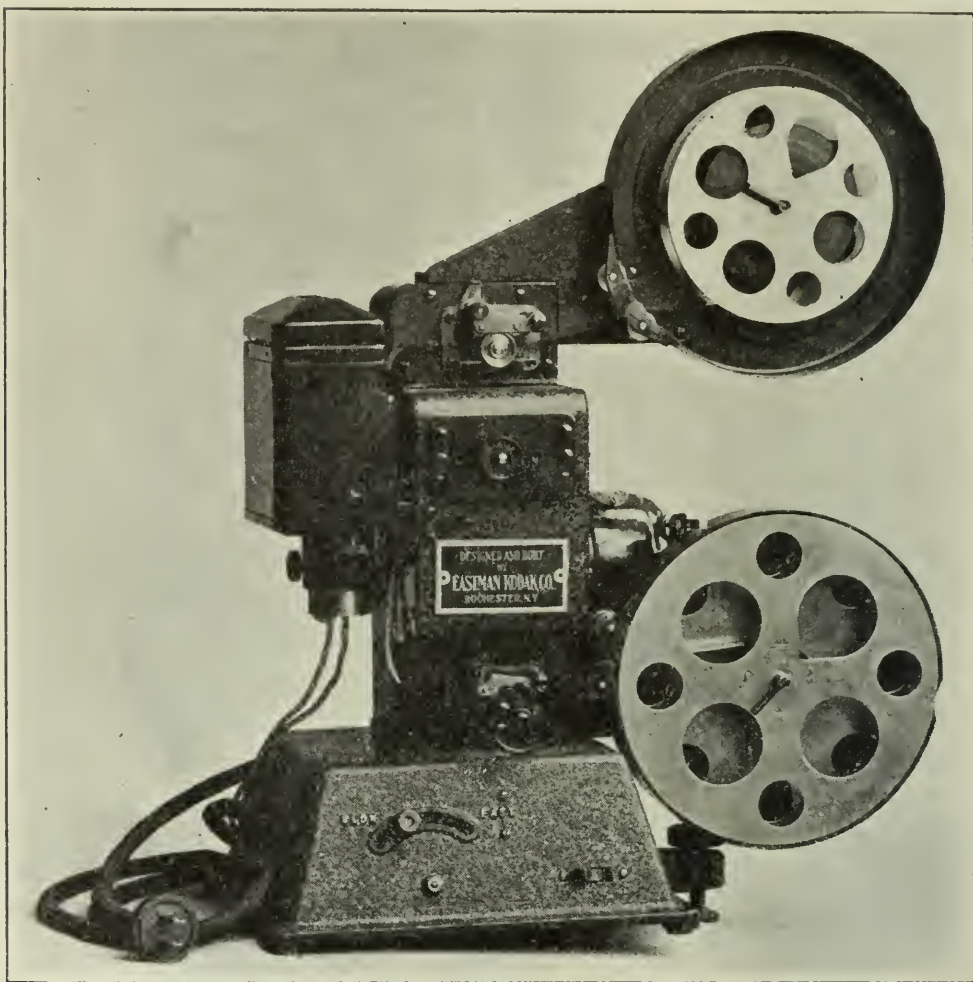
Cine Kodak on its tripod.

camera door can then be opened, the covers put on the spool of exposed film, and the spool removed and sent to the Kodak Company for development.

It is proposed to supply the camera either for use with the hand crank or with an electric motor attachment by which it can be cranked by the aid of a storage battery of very small size

carried by the user. When cranked by hand, the camera is used on a special tripod made to be as light and yet as rigid as possible, the tripod head being made to rotate and to move in a vertical direction for the convenience of the operator (Fig 6). It is not intended that the tripod head should be used to produce panoramic

FIG. 7.

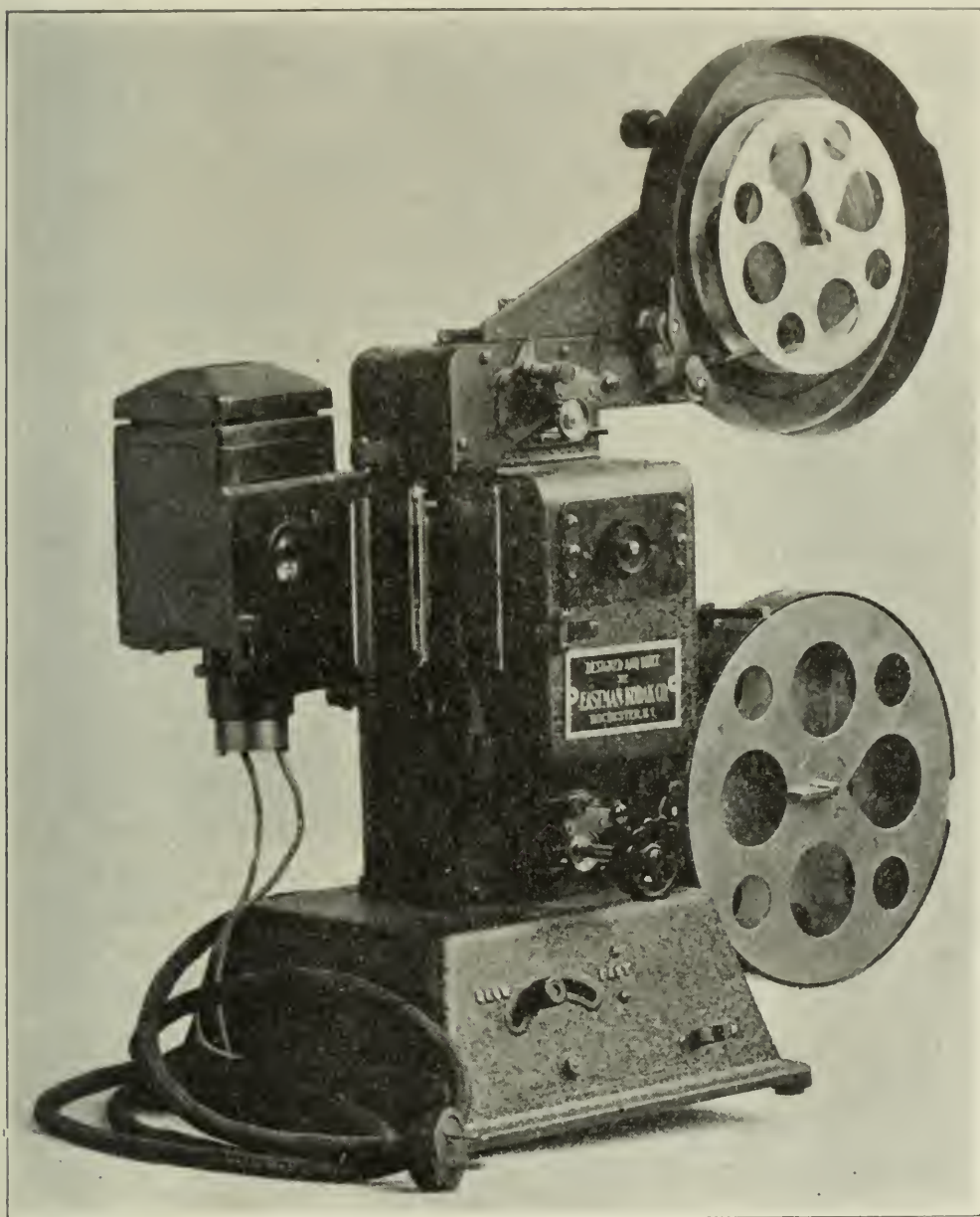


Kodaloscope projector.

pictures by rotating while the camera is being cranked. It is extremely difficult to do this smoothly, and the result when obtained rarely gives a pleasing impression when projected. A rotating head is necessary to enable the camera to be moved in direction rapidly in order to follow objects in the field. When the camera is used with the electric motor, it is not necessary to use a tripod, though it is convenient to rest the camera upon

something, and for this purpose a simple walking stick has been devised with a screw which fits into the tripod stick of the camera.

FIG. 8.



Kodascope with lamp house open.

This makes it possible to rest the camera and hold it steadily by the hand. The weight of the camera loaded is eight pounds; with the motor, ten and one-half pounds. The weight of the storage battery is two and one-half pounds, and of the tripod with

its special head, nine pounds. The camera on the tripod thus weighs seventeen pounds and the motor-driven camera with the storage battery, thirteen pounds. After the film has been developed, the positive is ready for projection.

The projector, which is called by us the "Kodascope," is, like the camera, a standard projector of the highest grade with such changes as are necessary to make it suitable for use by amateurs and for the small film (Fig. 7). The mechanism is of the same claw and cam type as the camera. The film, which is usually assembled in 400-foot reels, which are equivalent to 1000-foot standard reels and last for sixteen minutes on the screen, is placed on the upper shaft and the film is threaded on to an upper sprocket which feeds the film in a loop to the gate (Fig. 8), then through the lower sprocket to the take-up reel, which is placed on the bottom shaft. The Kodascope is driven by a motor, and the light is supplied by a mazda lamp through a condenser which is attached just behind the gate. The lens is of very high aperture, specially designed and built by us, and has a focusing mechanism of a convenient type. This high aperture lens and efficient condenser system give a bright image on a screen with a small lamp, and for home use the apparatus is arranged to give a satisfactorily bright screen of $4\frac{1}{2}$ feet in width, the two standard sizes of screens for home or classroom use being $30'' \times 40''$, which is large enough for the ordinary room, and $40'' \times 54''$, which is preferable for very large rooms or classrooms. By changing the lamp house and attaching a more powerful lamp with a special condenser system, a school can use a seven-foot screen and obtain ample light on it.

The Kodascope is entirely automatic in its operation. Once a film is threaded, there is no need to go near the machine until the film is exhausted, so that the operator is quite unnecessary, and the user can sit at ease among his friends while his pictures are being shown. The machine uses a lens of two-inch focal length and fills the $30'' \times 40''$ screen at eighteen feet distance and the $40'' \times 54''$ screen at twenty-four feet distance. The weight of the Kodascope projector with its motor ready for use is twenty-three pounds.

The quality of the picture depends upon three points: The optical perfection of the systems used in the camera and projector, on which depends the sharpness of the pictures that are taken:

the mechanical perfection, on which depends the steadiness of the pictures on the screen; and the photographic quality of the emulsion and the process used, on which depends the faithfulness with which the brightnesses in the light intensities in the original pictures are reproduced and the consequent fidelity to nature and also the appearance on the screen as regards any structure or graininess.

Now, when a small film is used for amateur photography, the

FIG. 9.



On left, small image marked A; on right, enlargement of small image to 55 diameters showing graininess.

accuracy required on all these accounts is increased, although fortunately the strains both on the film and on the mechanism are decreased. The lenses must be of the highest quality, since the small pictures will be enlarged to a greater degree than big pictures and must consequently be sharper. The mechanical accuracy must be higher, since any failure in perfection of register will be perceptible. The photographic quality must be at least as good if the user is to be satisfied with the result he is to get.

A number of inventors have designed cameras and projectors for amateur use in which the pictures were much smaller than those used on the standard film. The chief difficulty which is introduced when small pictures are used is the graininess which such a small picture shows when it is enlarged upon the screen.

A photographic image of any kind is composed of small clumps of the microscopic silver grains, and when it is very much enlarged these clumps show and give a structure to the image. In Fig. 9 we see at the left, at *A*, a very small image, and on the right the same image enlarged fifty-five diameters. It will be seen that the detail of the image is entirely lost owing to the graininess shown. The graininess in ordinary motion pictures is very slight but is visible when the observer stands close to the screen, and it is clear that if much smaller pictures are to be used and enlarged to the same size on the screen, the results would be greatly inferior to those obtained by the use of standard apparatus and that unless something can be done to diminish the graininess, the results would not be satisfactory in comparison with the pictures shown at the theatres. Moreover, even when a smaller film is used the cost, although diminished, is still high; a negative must be developed and a positive printed from it. This printing requires very skilled work. It is rare in standard motion picture practice for the first print from a negative to be entirely satisfactory, and to get a single print of high quality from every negative would be very difficult. The use of a small film treated like the regular film would, therefore, present two difficulties—high cost or low quality of results and the graininess of the image.

The ideal process for amateur use would clearly be one in which the original picture was available for projection on to the screen. In still photography it is an advantage to make negatives, because usually a number of prints are required from a single picture, but in motion picture work in most cases an amateur is interested in getting only a single print, and there are great advantages in a process which enabled a positive to be obtained by the direct treatment of the original exposure. The preparation of positives direct is well known in photography. The usual method is to develop the exposed image and then to dissolve out the silver in a "bleaching" bath, as it is called, which oxidizes the silver and leaves the undeveloped silver bromide intact. After exposure to light, this remaining silver bromide is developed in its turn and this gives a positive. This process has two disadvantages: It can give satisfactory results only through a very small range of original exposures because, if the exposure is too low, the amount of silver halide undeveloped is correspondingly large, and the final image is dense, while if the first exposure is heavy, there is not

enough silver salt left to form a satisfactory image. It is also dependent upon very exact evenness of coating. If the coating is too thick, then the whole positive will be overlaid by a deposit of silver which the first exposure could not reach, and if it is too thin, there will not be sufficient silver to give density in the final image. Variations in the evenness of coating will show very badly in the finished picture. As the result of a great deal of research work, a process was devised in our research laboratory which overcame these disadvantages. This process is the subject of an application for a patent, and its exact nature cannot there-

FIG. 10.



Enlargement from standard film and Kodascope positive to same magnification to show relative graininess.

fore be revealed at the present time. But it is possible now to obtain first-class positives upon coatings of any thickness whatever, the density not being dependent upon the evenness of the coating, and the control over variations of exposure quite as good as is possible if a negative be developed, and a positive be printed from it in the ordinary way. Moreover, these reversed pictures were found to be astonishingly free from graininess. The graininess is due to the large clumps of silver halide grains present in the emulsion. These large clumps are more sensitive to light than small or widely separated grains, and therefore when a short exposure is made, the large clumps are the first to become exposed. These are removed in the reversal process, and the final image is

made up of the grains of the least sensitiveness. Since these are the smallest grains and the smallest clumps of grains, such a direct positive image shows very little graininess. In Fig. 10 there is shown at the left, an enlargement from a standard motion picture print, and on the right the same scene taken on the small film and enlarged until it is the same size as the picture taken on the standard film. It will be seen that the small film is so free from graininess that a picture of the same size shows very little more graininess than if it had been made by the standard process.

The development of the film is quite a complicated process and requires very special and complicated equipment since the film has to go through a great number of treatments compared with the simple operation of developing and fixing to which motion picture film is usually exposed, and for this reason it has been decided that for the present, at any rate, the Kodak Company should undertake this work itself, and it is installing equipment which will make it possible to finish all the film that can be taken with the cameras in use.

Naturally, many amateurs will wish to have more than one print for some special reason, and this is provided for by the use of a special printer in which a positive can be duplicated, the duplicate being reversed into a positive in the same way as the original picture. In this way, it is possible to obtain duplicates at the same cost as the original picture, and though this is somewhat higher than the cost of making prints from an ordinary negative, there is no question that the use of the reversal process will greatly cheapen the production of motion pictures by amateurs. The small pictures can be enlarged in special printers to make pictures of the standard size required for theatres. This will no doubt not be required very often, but what will be done to a very large extent is that the pictures of standard size will be reduced to make the small prints suitable for projection in the Kodascope.

Fig. 11 shows Kodascope film side by side with the standard film. The Kodascope film was standardized as being 16 mm. wide compared with the standard width of 35 mm. The picture is 1 cm. \times $\frac{3}{4}$ cm. or 10 mm. \times $7\frac{1}{2}$ mm. compared with the standard picture of 1 inch \times $\frac{3}{4}$ inch, so that the area of the picture is approximately one-sixth of that of the standard picture. The film has only one perforation on each side per picture, while the

standard has four perforations. This has the advantage that it is impossible to misframe the picture. If it is framed at all, it must be framed right on the screen. It will be seen that five pictures on this small film occupy the same length as two pictures on the standard film. The small film, therefore, has forty pictures to a foot whereas the standard film has only sixteen pictures per foot, and while a foot of standard film lasts only a second on the

FIG. 11.



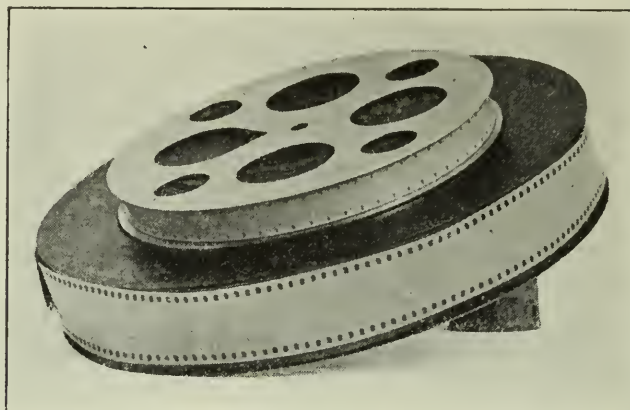
Kodascope film side by side with standard film.

screen, a foot of the Kodascope film lasts two and a half seconds. The spool used in the Cine Kodak takes 100 feet of the small film, corresponding to 250 feet of the standard film, and the Kodascope projector reel takes 400 feet, corresponding to the standard thousand-foot projection reel, which runs for sixteen minutes (Fig. 12). The small size of the Kodascope film naturally makes its cost much less than that of standard film. It costs approximately fifteen cents to take a negative, develop it, and make

one print on standard film for each second on the screen; that is, for each foot of film, so that to make a standard film of 1000 feet will cost \$150. The Kodashcope film will cost about two and a half cents a second, so that a reel running for one thousand seconds will cost \$24. The cost of the film which is rented will, of course, be correspondingly lower in the smaller sized film, so that an evening's entertainment at home will be obtainable for a very reasonable sum.

In order to get some idea of what this means to the amateur, it is necessary to remember how long a picture should be. Experience has shown that a view of a stationary object, or one in which

FIG. 12.



Standard reel and Kodashcope 400-foot reel.

the movement is repeated, such as a water fall or a game, and in which there is no continuity in the action, should last on the screen for between 5 and 10 seconds. This may seem short, but trial shows that if a scene of this type lasts for more than 10 seconds the audience wearies of it. When taking pictures with the Cine Kodak, therefore, it is desirable to give about 7 or 8 seconds' exposures to each scene, moving the camera from one point to another in order to get variety. The cost, therefore, of a single scene taken with a Cine Kodak is about twenty cents, and this compares favorably with the cost of taking an ordinary kodak picture, developing the negative, and making one print. On the whole, it appears as if amateur cinematography with the Cine Kodak will not be more expensive to the user than is still photography.

The film base used for making the Kodascope film is the slow-burning film made from cellulose acetate. While the cellulose nitrate film commonly used in motion pictures is entirely safe for theatrical work where proper precautions are taken to prevent

FIG. 13.



Enlargement of single small picture.

any risk of film fires and to quench a fire should it arise, the introduction of such film into the home or school is most dangerous, and one of the great advantages of using a special size of film is that it will not be possible to obtain this film in the fast-burning nitrocellulose stock. For the same reason, though to a lesser degree, it is an advantage that this new film cannot be cut from

film of standard size by any simple operation. Several small projectors that have been built recently have been made to take half-width film, to be obtained by slitting standard perforated motion picture film in half. While, of course, it is intended that slow-burning stock only should be used for this purpose, there is always the danger that some one would be tempted to use the cheaper nitrate stock and to slit it in half for use in the narrow width. The same objection applies with much greater force to the use of projection machines taking film of standard width. It is probable that in the near future there will be a number of projectors on the market and possibly some cameras also taking the 16-mm. film, so that the 16-mm. size may become a standard throughout the entire trade for small film used for amateur cinematography just as the professional $1\frac{3}{8}$ -inch film, used first by Lumière and Edison, became the standard for all motion picture work.

The single small pictures taken on the Cine Kodak can be enlarged, and so fine is the grain and so good the definition that the results of enlargements of these extremely small pictures, which, if examined in the hand, need a microscope to see the detail, are of surprising quality. One of these enlargements is shown in Fig. 13.

The first equipment to be put on the market by the Kodak Company will be in the form of an entire outfit for taking and projecting the pictures. It will include the camera with its tripod and tripod head, the Kodascope with the screen, and the necessary accessories, such as a device for joining the films together. The price has not been definitely settled yet, but it will be in the neighborhood of \$300, and with the outfit an amateur will be equipped to take his own pictures and project them or those taken by other people.

The introduction of motion pictures into the home will, of course, produce a demand for pictures other than those taken by the owner of the machine, and we are arranging therefore to supply for the Kodascope a library of films made by the reduction of standard reels to Kodascope size. We hope in the next year to have several hundred subjects available, including scenic pictures, stories for children, and pictures of all kinds of a type suitable for use in the home. We believe that the spreading use of the motion picture at home will increase the public interest in

the motion picture and will rouse the interest of many people who have not, up to the present, been regular attendants at the motion picture theatres, so that they will follow the progress of the art and will take a real interest in the development of pictures as shown in the large theatres. Just as the widespread use of photography by the amateur has been the chief contributing cause to its marvelous development in the last thirty years and to its extension to every field of human activity, so I believe the use of the motion picture by photographers throughout the world will make possible developments in the art of motion picture that are at present undreamt of, and that the use of the motion picture in schools, institutions, and homes has a future to which the Cine Kodak and Kodascope will contribute in no small degree.

Wilhelm Hallwachs. OTTO WIENER. (*Physikal. Zeit.*, Nov. 15, 1922.)—On the 20th of June, 1922, this distinguished German physicist died. His name is inseparably linked with the effect that he discovered. Shortly after Hertz had performed his epoch-making investigations, proving the existence of electrical waves from which wireless telegraphy and telephony have sprung, Hallwachs found that ultra-violet light falling on a zinc plate negatively charged causes it to lose its charge. If the plate were positively charged it was not so discharged. Paper after paper brought to light the phases of this effect, but there came a pause of fourteen years in his investigations on this subject. About 1904 he resumed his photoelectrical activity and succeeded in solving many questions in this field. "Question follows question and step by step each is answered with thoroughness by means of experimental skill." This investigation is only the best known of his contributions to physics.

He was the son-in-law of Friederich Kohlrausch, whose assistant he was at Strasbourg. There are American students who will recall with pleasure their acquaintance with this genial and gifted experimenter.

G. F. S.

Discharge of Electrons from Electrodes Nearly in Contact. FRANZ ROTHER. (*Physikal. Zeit.*, Oct. 15, 1922.)—In 1911 this Leipzig physicist showed that a current flows from one electrode to another even with small differences of potential, provided the distance separating the two is exceedingly small. When the interval is as short as a light wave, 10 volts cause a current of 10^{-14} ampere to flow across. The experiments leading to this result were conducted in air at pressures of 760 and of .5 mm., and pressure appeared not to influence the result. To test this conclusion it was desired to repeat

the investigation, using the highest attainable vacuum. The problem was then to devise a way of mounting two electrodes in such a vacuum so that their distance apart could be varied and, more than that, measured with great accuracy. Two methods of moving the electrodes were available, electrostriction and the bending of a metallic membrane. One electrode was attached to an iron rod whose length was varied by changing its magnetization. This plan was defective when it was needed to bring the electrodes into actual contact. In the second method the electrode was carried by a platinum membrane whose form was governed by the difference between the pressure in the tube and the external pressure. This met the requirements more completely than the former method. The measurements of distance were made by an interference arrangement. The electrodes were metal cylinders 4 mm. in diameter with polished hemispherical ends.

For platinum hemispheres of radius 20 mm. in a high vacuum, a current of about 5×10^{-14} amperes flowed from one electrode to the other, 250 millionths of a millimetre distant, when the difference of potential was 190 volts. The increase of current with voltage was rapid. Electrons appear to be driven out of the metal by a sort of "cold Richardson effect."

G. F. S.

The Thermal Effect of Vapors on Rubber. A. S. HOUGHTON. (*Proc. Phys. Soc.*, Dec. 15, 1922.)—Into carbon dioxide were plunged two exactly similar thermometers, the bulb of one of which had been covered with a thin film of rubber, left by the evaporation of a rubber solution. The latter instrument showed a higher temperature.

Lengths of copper and Eureka wire were soldered together, the kinds alternating. The first, third, fifth, etc., junctions were exposed to vapors while the even junctions were protected from them. Immediately on exposure a galvanometer joined to the series of wires indicated a sudden rise of temperature. This became zero as the exposure continued. Upon the withdrawal of the junctions there appeared a sudden cooling which in turn disappeared after a time. The vapors of chloroform, benzene, toluene, pyridine and oils of lavender and guaiacol showed the effect. Ammonia and carbon dioxide are known to pass through rubber. These gases showed the effect, but the heat developed was not great. Moist air gave the effect very clearly.

The greatest difference of temperature produced by the presence of the rubber was about one degree.

The heating of cellulose by water-vapor seems akin to the effect above described. "Rubber differs, however, from cellulose in its non-fibrous structure and wide range of action with vapors. So it is probable that only a part of the heat produced is due to the condensation of the vapor on the rubber, and the additional heat is supplied either by some form of chemical union, or by the formation of a solid solution between the vapor and the rubber."

G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

INVAR AND RELATED NICKEL STEELS.¹

[ABSTRACT.]

THIS circular is mainly a compilation of data obtained during the last thirty years by various investigators on the different properties of nickel steels. Particular attention is given to "invar," a nickel-iron alloy containing about 36 per cent. nickel and possessing an extremely small thermal expansivity at ordinary temperatures, the mean coefficient of linear expansion between 0 and 40° C. being on the order of 1 to 2 millionths. The results of investigations made on the various properties of the nickel-iron alloy series have been presented largely in diagrammatic and tabular form.

Following an historical account of the development of nickel steels and studies of their properties, the nature of the anomalies in behavior met with in these steels and characterized by their irreversible and reversible phenomena are discussed in the light of the results obtained on their various physical properties. The constitution and microstructure of these alloys are first dealt with, and next the rather extensive studies made on the magnetic properties. A magnetic transformation (Curie points) diagram has been plotted from the observations obtained magnetically, for the most part, by various investigators.

Anomalies in the change of electrical resistance with temperature are shown to be present in nickel-iron alloys. It is seen from the diagram for electrical resistivity at ordinary temperatures, plotted from data obtained on pure ferro-nickels, that there is a sharp increase in resistance for those alloys containing about 30 to 35 per cent. nickel—the resistivity of invar being on the order of 80 microhms-cm.

The anomalous behavior in the thermal expansion of nickel-iron alloys at various temperatures is illustrated by a number of diagrams, and the rule of corresponding states formulated by Guillaume has been applied in interpreting some of the results. The degree of thermal expansivity reaches a minimum in alloys

* Communicated by the Director.

¹ Circular No. 58, second edition, price thirty cents.

with about 36 per cent. nickel (and 0.4 per cent. manganese and 0.1 per cent. carbon), and the position of this minimum may be modified by the presence of added elements as chromium, etc., and also by thermal or mechanical treatment. The theories advanced as an explanation for the anomalous behavior in the expansibility of nickel steels are briefly dealt with. In addition to the principal characteristics of thermal expansion, there are certain secondary phenomena of a transitory and of a progressive nature occurring over small ranges of temperature or even at constant temperatures over a long period of time which affect the constancy in the dimensions of the invar. An aging process or special heat-treatment is employed to reduce these secular changes to a minimum. The cause of this instability of nickel steels has been found to be due to the presence of carbon.

The thermal conductivity and specific heat of nickel-iron alloys show minimum and maximum values, respectively, at about 35 per cent. nickel.

Some data on the mechanical properties and also Brinell and Shore Scleroscope hardness of nickel steels, with the nickel content ranging up to about 50 per cent., are given in tabular and in diagrammatic form. The tensile properties of invar may run as follows: Tensile strength, 50,000–100,000 pounds per square inch; elastic limit, 30,000–70,000 pounds per square inch; elongation, 25 to 50 per cent.; and reduction of area, 40 to 70 per cent.

Nickel steels present anomalies in the elastic modulus, corresponding closely to those found in thermal expansion. It has been found that the degree of anomaly can be reduced in very large measure by means of suitable additions made to the alloy, namely, about 12 per cent. chromium or its equivalent, this alloy having recently been introduced under the trade-mark "Elinvar." This is of practical importance in the construction of watches and chronometers, where the degree of error with variations of temperature and consequent need for compensation may be made very small.

Resistance to corrosion by fresh and sea water and acid liquors increases with the proportion of nickel. An alloy containing about 18 per cent. may be regarded as practically non-corrodible. The resistance of invar to oxidation, while very much greater than that of ordinary steel, is not perfect, therefore it is advisable to

coat an invar instrument with a protective coating as vaseline, if it is to be exposed for a long time in a moist atmosphere.

The extent and nature of applications of nickel steels are discussed. A list of makers of nickel steels and dealers in nickel steels of minimum thermal expansivity in America and also a selected bibliography are included.

RECOMMENDED SPECIFICATION FOR QUICKLIME FOR USE IN CAUSTICIZING.²

[ABSTRACT.]

THE manufacture of caustic alkali consumes a large tonnage of quicklime annually. For this purpose a very pure grade of lime is required. Purity is determined not by the total content of calcium oxide, but rather by the content of calcium oxide which is available in the process for which the lime is used. A careful study of the requirements of the users of the quality of lime which is actually being used and of the possibilities of production have led to the establishment of 85 per cent. as a fair standard for available lime. Unlike most materials which are bought on specification, chemical lime is more valuable if it has a higher degree of purity than that required by the standard and less valuable if it has a lower degree. For this reason we have recommended that a bonus and penalty clause be inserted in the contract in order to take care of variations from the 85 per cent. While the material is less valuable, but can still be used if the purity falls below the standard, there is a point reached eventually when the value of the material becomes such that it is poor economy to use the lime for this purpose. A careful survey of the situation has led us to set this figure at 70 per cent. In working up the details of this specification the bureau has been assisted by an Interdepartmental Conference on Chemical Lime, composed of representatives of various government agencies. The specifications have been partially approved by the National Lime Association, representing the producers, and by the Technical Association of the Pulp and Paper Industry, representing the largest group of consumers of this kind of lime.

² Circular No. 143, price five cents.

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RECOMMENDED SPECIFICATION FOR LIMESTONE AND
QUICKLIME FOR USE IN THE MANUFACTURE OF
SULPHITE PULP.³

[ABSTRACT.]

IN the manufacture of sulphite pulp the wood is cooked with a solution of calcium bisulphite. This solution may be prepared in two ways, either by permitting sulphur dioxide to pass upward through a tower filled with limestone and allowing water to trickle down over the stone, or by passing the sulphur dioxide through milk of lime contained in a tank. In the former process high-calcium limestone is preferred, because limestone containing much magnesium carbonate is not dissolved uniformly and is thus apt to fall to pieces and stop the circulation. In the latter process a high-calcium quicklime is preferred for the manufacture of the milk of lime, because the magnesia is more soluble than the lime in the sulphur dioxide solution and a liquor having higher strength can thus be prepared. It is quite possible, however, to use a high-magnesium stone in the tower process or a high-calcium lime in the milk-of-lime process. The specifications, therefore, cover both high-calcium and high-magnesium limestone and quicklime on the basis of about 95 per cent. purity.

The Fluorescence and Coloration of Glass Produced by Beta Rays. J. R. CLARKE. (*Phil. Mag.*, April, 1923.)—Three specimens of soda glass tubing were kept in radium emanation until they had acquired a rich brown color and had ceased to fluoresce. Each specimen was divided into four parts. When a part was put into an oven it began to fluoresce and continued to do so until the brown color had disappeared. The hotter the oven the shorter the time needed to remove the color and also the more intense the fluorescent light. One specimen lost its color in the following number of minutes at the temperatures designated, 110°, 13 min.; 180°, 3 min.; 235°, 1.5 min.; 350°, .75 min. In one case at a temperature of only 95° the fluorescence lasted fifteen hours. "The decoloration of the glasses, therefore, appears to be connected with a change in the state of molecular aggregation, coloration being the reverse process. As both coloration and decoloration were accompanied by fluorescence, it is probable that the fluorescence is due to this change."

Of nineteen kinds of glass examined, fourteen turned brown and the rest purple. All that turned purple had manganese in them. The others contained none of this element.

G. F. S.

³ Circular No. 144, price five cents.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

AN ADAPTATION OF THE THALOFIDE CELL TO THE MEASUREMENT OF PHOTOGRAPHIC DENSITIES.¹

By A. L. Schoen.

IN photographic research, it is frequently necessary to measure low densities with great accuracy. The usual visual methods for measuring density have been found inadequate for this purpose. Tests made with thalofide cells to determine the conditions for high sensitivity and stability show that this instrument can be adapted as a physical photometer for the measurement of these densities.

Changes in sensitivity with applied voltage and intensity of illumination were observed. From these data the best voltage and illumination were determined and maintained constant on the cell. Densities were determined (using the inverse square law) by moving the source of illumination to produce zero deflection in a sensitive galvanometer for each step of the sensitometric strip.

Results obtained thus far indicate that this method can be used with advantage in problems involving the measurement of very low densities and small density differences and that densities as low as .005 (± 99 per cent. transmission) can be measured with a fair degree of certainty.

SIZE-FREQUENCY DISTRIBUTION OF GRAINS OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS. V.—SYSTEMATIC CORRELATION.²

By E. P. Wightman, S. E. Sheppard, and A. P. H. Trivelli.

A SERIES of photographic emulsions has been prepared of which a correlation between the grain and sensitometric characteristics shows an apparently close relationship. These emulsions are strictly comparable because practically all the factors in their preparation were under control, only one being varied so as to progres-

* Communicated by the Director.

¹ Communication No. 171 from the Research Laboratory of the Eastman Kodak Company and published in *J. Opt. Soc. Amer.*, June, 1923, p. 483.

² Communication No. 172 from the Research Laboratory of the Eastman Kodak Company and published in *J. Phys. Chem.*, May, 1923, p. 466.

sively increase the speed of the emulsions in the series, and because equal weights of emulsion containing in every case the same amount of silver halide by weight were coated on the plates. The equations which represent the grain-size-distribution of these emulsions show a steady transition from a steep exponential, $y = y_0 e^{-kx}$, to a flat, widely spread Gaussian type, $y = y_0 e^{-k(x-\alpha)^2}$. That is to say, in passing through the series from the slow to the comparatively fast emulsion the parameters y_0 and k steadily decrease, while the parameter α , which is zero in the first two examples, then steadily increases.

THE RESISTIVITY OF VARIOUS MATERIALS TOWARDS PHOTOGRAPHIC SOLUTIONS.³

By J. I. Crabtree and Glenn E. Matthews.

OF the metals and alloys, lead, nickel, Niaco, and monel are the most resistive to photographic solutions, but are suitable only for developing and washing apparatus. Toning baths attack all metals. With fixing baths a protective layer of silver plates on the metal tends to retard corrosion. Monel is quite satisfactory for clips, hangers, and small tanks which are not permanently in contact with the solutions. Salts of copper or stannous tin cause bad developer fog, so that copper or tin alloys containing these metals, such as solder or brass, should not be used in contact with developers. Metallic contact of two different metals or alloys causes electrolysis which hastens the rate of corrosion. Lead-lined tanks are satisfactory for developers and fixing baths if the joints are lead burned. Lead piping is suitable if the joints are wiped.

Of the non-metallic materials, glass, enamelled steel, well-glazed earthenware, hard rubber and wood resist all photographic solutions. Porous earthenware, rubber composition, and impregnated products disintegrate as a result of crystallization of hypo or other salts in the pores of the material. Small dishes should be made of glass, enamelled steel or hard rubber. Deep tanks for motion picture work may be of wood (cypress), lead-lined wood, Alberene stone or slate, well-glazed stoneware, or Portland cement. Piping should be of lead, hard rubber, or glass.

³ Communication No. 176 from the Research Laboratory of the Eastman Kodak Company and published in *Ind. Eng. Chem.*, July, 1923, p. 666; *Brit. J. Phot.*, June 15, 1923, p. 366.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

COMPOSITION OF FREE FATTY ACIDS OF COTTONSEED OIL.¹

By George S. Jamieson and Walter F. Baughman.

[ABSTRACT.]

THE fatty acids of cottonseed oil and of peanut oil are set free by hydrolysis in practically the proportions in which they occur as glycerides in the oils. The same probably is true of the fatty acids in all other vegetable oils.

GROUNDING COTTON GINS TO PREVENT FIRES.²

By Harry E. Roethe.

[ABSTRACT.]

THE installation of grounding systems for removing electrostatic charges in cotton gins is one of the most effective means of preventing fires in gins. The U. S. Department of Agriculture has developed an inexpensive and effective grounding system. Many insurance companies in the South give lower insurance rates for gins having a proper grounding system.

CHEMICAL, PHYSICAL, AND INSECTICIDAL PROPERTIES OF ARSENICALS.³

By F. C. Cook and N. E. McIndoo.

[ABSTRACT.]

THE Bureau of Chemistry has determined the chemical and physical properties of a large number of commercial arsenicals and a large number of arsenicals prepared in the laboratory. It has also determined the compatibility of various mixtures of arsenicals with other insecticides and fungicides. The Bureau of Entomology has determined the comparative toxicity of the same arsenicals.

* Communicated by the Chief of the Bureau.

¹ Published in *Cotton Oil Press*, 7 (June, 1923) : 35.

² Issued as *U. S. Dept. Agr. Cir.* 271 (May, 1923).

³ Issued as *U. S. Dept. Agr. Bul.* 1147 (June 8, 1923).

From this work the conclusion is drawn that a chemical analysis of an arsenical does not give sufficient data to judge satisfactorily its insecticidal properties and a toxicity study alone does not show that an arsenical is suitable for general insecticidal purposes. Both a chemical analysis and a toxicity study are necessary to show whether or not an arsenical is a satisfactory insecticide.

EFFECTS OF TREATING MATERIALS AND OUTDOOR EXPOSURE UPON WATER RESISTANCE AND TENSILE STRENGTH OF COTTON DUCK.⁴

By T. D. Jarrell and H. P. Holman.

[ABSTRACT.]

WATERPROOFING materials frequently hasten deterioration in the strength of canvas exposed to the weather. Waterproofing treatments free from mineral pigments made canvas after exposure weaker than the untreated canvas after exposure. Preparations containing an excess (over 50 per cent.) of asphalt or coal-tar pitch usually caused less deterioration in strength and gave greater water resistance than other treatments free from mineral pigments. The addition of mineral pigments to certain waterproofing preparations which have a deteriorating effect on canvas when exposed to the weather materially reduced this effect, and in some instances made the treated canvas stronger than the untreated canvas after exposure. Usually the addition of pigments did not interfere with water resistance and sometimes materially increased the water resistance.

On Tidal Stresses and Continental Displacements. H. H. POOLE. (*Phil. Mag.*, March, 1923.)—Eddington has given .001 second as a probable value of the increase in the length of a day produced by the action on the earth of tidal forces during a century. Using the moment of inertia of the earth about its axis (9.74×10^{44} gram sq. cm.) the author calculates that to produce the specified lengthening of the day, a uniform force acting over the entire surface of the earth would be adequate if it amounted to the weight of a kilogram per square kilometre. This force is too small to have produced much displacement of the continents. "It would seem then that, if tidal stresses have played a part in the history of the continents, they must have done so in past epochs, when, owing to crustal weakness or the closer proximity of the Moon, they were far more powerful than at present." G. F. S.

⁴ Published in *J. Ind. Eng. Chem.*, 15 (June, 1923): 607.

NOTES FROM THE U. S. BUREAU OF MINES.*

COMPARISON OF GAS MASKS, HOSE MASKS, AND OXYGEN-BREATHING APPARATUS.

By S. H. Katz and J. J. Bourquin.

THREE types of respiratory apparatus, namely, gas masks, hose masks, and self-contained oxygen-breathing apparatus, are now commonly used for protection from noxious gases, vapors, and smokes or mists, but no particular type can be selected as best for all conditions. Many factors must be considered in connection with each situation, so that each must be considered as a problem in itself.

Gas masks are the simplest and easiest to wear, also the least cumbersome, but they protect only in comparatively low concentrations of noxious gases and should never be used where the air contains less than 16 per cent. of oxygen. Special masks give protection from one gas or class of gases, but may give no protection against another gas or class of gases.

Hose masks protect in any irrespirable atmosphere, but are somewhat cumbersome, the length of hose limiting the distance a wearer may go from fresh air. They are serviceable also where a supply of pure air moves with the wearer, as where a locomotive engineer in a smoky tunnel is using a hose mask supplied with air from the compressed air line of the locomotive. Hose masks consume no chemicals or materials and so are not limited in the time they may be used.

Self-contained oxygen-breathing apparatus protect in any irrespirable atmosphere, but their weight is cumbersome, they can be used only by trained men, and frequent attention must be given them to maintain good working condition. On the other hand, they are the only safe means for exploring mines and other places filled with irrespirable gases in high concentrations.

More complete statements concerning the properties of each apparatus are given in Serial 2489, recently published.

* Communicated by the Director.

RESULTS OF ASSAYS OF THE NEW ALBANY OIL-SHALE.

By John R. Reeves.

IN a general survey of the oil-shale resources of Indiana, other papers have already been published which present data with reference to the following points: (1) Distribution of the New Albany shale; (2) amount of shale available; (3) homogeneity and thickness of the formation; (4) amount and quality of the oil obtained from the shale; (5) nitrogen content of the shale; (6) extractibility of the shale and its amenity to breaking; (7) some economic factors bearing upon the utilization of the shale; and (8) other miscellaneous factors and data. In the future, technical work on other phases of the general problem is expected to be done with the object of making a complete survey of this resource which is of much potential importance to the State and Nation.

There was recently completed an analytical survey of samples systematically collected from the outcrops, representing complete sections of the New Albany formation at different points in the district.

Each sample was tested for oil yield, water yield, specific gravity of crude oil, distillation of crude oil (atmospheric distillation ending at 275° C.), unsaturation of tops (fraction boiling to 275° C.), carbon residue of residuum from atmospheric distillation, yield of scrubber naphtha, and percentage of nitrogen.

The oil yield varies from 4.8 gallons per ton to 15.7 gallons per ton. The average yield for all samples is 10.3 gallons per ton. The specific gravity of the crude oil varies from 0.924 to 0.955. The average of all samples is 0.943.

The unsaturation of the tops varies from 39.0 per cent. to 45.0 per cent., the average of all samples being 42.1 per cent.

The carbon residue of the residuum from the atmospheric distillation (end point 275° C.) varies from 4.95 per cent. to 7.67 per cent., the average of all samples being 6.3 per cent. The amount of scrubber naphtha, at the rate of retorting used in this work, varies from 0.31 gallon to 1.83 gallons per ton.

The total nitrogen of the New Albany shale varies from 0.107 per cent. to 0.777 per cent., the average for 15 samples being

0.381 per cent., equivalent to a theoretical yield of 35.89 pounds of ammonium sulphate per ton. Further details are given in Serial 2492, just issued.

ATMOSPHERIC CONDITIONS IN UNION PACIFIC TUNNELS.

By S. P. Kinney.

THE Department of the Interior has recently investigated the atmospheric conditions in tunnels of the Union Pacific Railroad in Utah and Wyoming, by observations made from the cabs of freight locomotives. This work was conducted by the Bureau of Mines at the request of, and in coöperation with, the Union Pacific Railroad Company, and was brought about by several accidents to members of engine crews, while passing through tunnels, from pollution of the tunnel air by exhaust gases from freight locomotives.

As a result, the causes of the gassing accidents were determined, the composition of the air in locomotive cabs while passing through railroad tunnels; the effect of these conditions on the engine crew; and recommendations made for protection of the men so exposed.

Gas samples and temperature readings taken in the cabs of locomotives were used in studying the atmospheric conditions to which the locomotive crews were exposed. The symptoms and the physiological effects produced in men exposed to the atmospheres encountered were studied. The pulse rates and body temperatures were taken, and determinations of the carbon monoxide content of the blood were made. Various methods for the prevention of gassing and for the protection of men therefrom were considered and tested; among which were the use of mechanical devices for deflecting the smoke away from the engine cab, and the use of various types of gas masks and breathing apparatus.

While this investigation is a part of the safety work of the Bureau of Mines in connection with hazards from atmospheres containing carbon monoxide, the results are of particular value to railroads operating steam locomotives through tunnels, and

are also valuable to other industries where atmospheres having poisonous gases or of a high temperature and humidity may be present. Further details are given in a recent publication.

THE PYRO TANNIC ACID METHOD FOR THE QUANTITATIVE
DETERMINATION OF CARBON MONOXIDE
IN BLOOD AND AIR.

By R. R. Sayers, W. P. Yant, and G. W. Jones.

It is of vital importance in all industrial and domestic accidents occurring at places where carbon monoxide might be suspected or where the symptoms are typical of carbon monoxide poisoning that a qualitative and preferably a quantitative determination be made (the extent of poisoning being of importance in deciding whether carbon monoxide was the direct or contributory cause) to show the presence or absence of carbon monoxide. This is indeed essential from a medical standpoint, as it aids in prescribing treatment and from a legal standpoint to insure justice in the claims that are often unjustly decided for want of positive evidence. Probably the best method of diagnosis is by examination of the subject's blood. Many methods for the detection of carbon monoxide in the blood have been developed, but owing to their various individual disadvantages have never come into common usage. Some of the quantitative methods are satisfactory with regard to accuracy, but require elaborate and expensive apparatus, special technic and training, or are too delicate and cumbersome for field use.

In view of the above an apparatus has been designed by the bureau, which gives accurate results in the field and laboratory, yet it is compact (can be carried in the pocket) and durable, and sufficiently simple in operation to be used without special training. By use of this method, it is possible to detect the presence of carbon monoxide in the blood in three minutes and determine the exact amount present within fifteen minutes, and on the basis of these findings, treatment administered. The method and apparatus should fulfill the needs of hospitals, industrial surgeons, safety engineers, coroners, departments of public safety, boards of health, and other allied organizations. Further details are given in Serial 2486, recently issued.

THE FRANKLIN INSTITUTE.

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MR. ANTHONY W. ROBINSON, 6 College Avenue, Haverford, Pennsylvania.

NECROLOGY.

Dr. Rudolph Hering was born in Philadelphia, February 28, 1847, and died in New York City on May 30, 1923. He was educated in the schools of his native city and obtained his technical training at the Royal Polytechnic in Dresden, Germany, from which he graduated in 1867. In 1868 he became Assistant Engineer at Prospect Park, Brooklyn. In 1869-71 he served in the same capacity in Fairmount Park, Philadelphia. From 1873 to 1880 he was Assistant City Engineer in Philadelphia. He then devoted his time to private practice and was Chief Engineer of the Chicago Drainage and Water Supply Commission from 1886 to 1888, and Consulting Engineer, Department of Public Works, New York City in 1889. He acted as Consulting Engineer for water supply and sewage works in about 150 cities, including New Orleans, Los Angeles, Tacoma, San Francisco and Honolulu. He was a member of the leading civil engineering societies of the world and the author of many reports on sewerage and water supply. Doctor Hering became a member of The Franklin Institute in 1867.

Dr. Adolph W. Miller, 400 North Third Street, Philadelphia, Pennsylvania.

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BOOK REVIEWS.

PRINCIPLES OF CHEMICAL ENGINEERING. By William H. Walker, Warren K. Lewis and William H. McAdams, Professors of Chemical Engineering at the Massachusetts Institute of Technology. 8vo, vii-609 pages, 156 illustrations and one plate. New York, The McGraw-Hill Book Company, 1923. Price \$5 net.

Chemical engineering and engineering chemistry are two very different topics. The latter relates to the analysis of engineering materials and has been for many years extensively treated in standard manuals. Chemical engineering, as a special branch of applied chemistry, is of comparatively recent

origin, but the enormous development of chemical industries has brought about a great expansion of the study of both practice and theory of procedures. Most handicrafts began in purely empiric methods; the study of the principles came much later. It was a characteristic of the ancient world that there was an almost complete separation of the scientist from the worker. The "philosophers," as they were called, disdained to mingle with the artisans, who were in large part slaves, or at least subject to severe masters, although in some directions, such as engraving and delicate work, the rarity of the special qualifications gave the worker a certain degree of self-assertion. Similarly to-day, the diamond-cutters constitute a powerful guild by reason of the highly specialized nature of their work.

The book in hand is not a technology. It does not discuss the procedures for the manufacture of particular substances, but treats of the principles of the standard processes that are employed in the plants in which the chemicals are made. The authors have, as stated in the preface, selected basic operations and have brought in the most modern data of physical chemistry to aid in the explanation of these procedures. The text, indeed, contrasts very strongly with that heretofore found in works on applied chemistry, mathematics being employed in giving quantitative features to the descriptions. In the presentation of these quantitative data, use is made of a unit termed the "pound mol." This is explained, together with many other important points in the first chapter on the "Elements of Industrial Stoichiometry." In this chapter the discussion of the calculation methods is very extensive. The authors regard the conversion of the metric units into the older form and *vice versa*, as essentially simple. This is encouraging to those who wish to see the bugaboo that has interfered with metric reform exorcised. The advanced character of the book is indicated by the title of the second chapter "Fluid Films." Chapters follow on flow of fluids and of heat, fuel and power, combustion, furnaces and kilns, gas producers, crushing and grinding, mechanical separation, filtration, vaporization, evaporation, humidity, humidifiers, drying and cooling; the final chapter being on distillation.

In the chapter on mechanical separation the discussion of the curious and comparatively recent flotation methods is very brief and no mention is made specifically of the oil processes. The brevity of the treatment of this branch of the subject is due to the fact that the book is an essay on the principles of the several procedures and not upon the application of them. The authors tell us that a great many flotation processes are in successful operation, but none of the many theories offered to explain the phenomena has been accepted as generally applicable. Rickard and Ralston in their work on flotation (Mining and Scientific Press, 1919) gave an interesting history of the development of the procedure, and find—as might be expected—some reference to the practice in Heroditus. An interesting and useful application of oil-separation is described in Williams' work on the diamond mines of South Africa. Oil-separation was found very serviceable in separating the rough diamonds from other minerals.

Extensive discussion is made of the processes of combustion and of the construction of furnaces and kilns. The advantages and disadvantages of

powdered and liquid fuels are presented clearly. The work is elaborately illustrated with representations of apparatus and with diagrams. The text is clearly and carefully written and presented in good form. The book is a most valuable contribution to a field which is of great and rapidly growing importance, and is another item in the evidence that the American scientist is getting out of the necessity of seeking an education abroad.

HENRY LEFFMANN.

COURS DE CHIMIE INORGANIQUE. By F. Swarts, Professor at the University of Genth. Third edition, revised and enlarged. 8vo, 714 pages, contents and index. Brussels, M. Lamertin. Fifty francs net, in paper.

COURS DE CHIMIE ORGANIQUE. By the same author. Third edition, revised and enlarged. 8vo, 652 pages, contents and index. Same publisher. Fifty francs net, in paper.

These two books present a comprehensive survey of the important data of chemistry and embody the late developments in atomic and molecular structure and the phenomena of isotopy and radioactivity. Favorable criticism can be made of the material presented, of the method of arrangement and the explicitness of the descriptions. Distinction is emphasized between physical and chemical phenomena, experiments long known and used being described for illustrations thereof. Of late years chemists and physicists have been drawing together and the two departments of science are practically now interpenetrating. There is a great deal of old-fashioned experimenting given. Under oxygen, for instance, it seems inadvisable to take up space describing the decompositions of manganese dioxide and potassium chlorate separately, and then describing the method in which they are mixed. The latter is the only one used in laboratories or at lectures when small amounts of the gas are desired, while the commercial preparation is by entirely different procedures.

Being third editions, the books do not need an extended review. They have been before the Belgian scientific public long enough to have their merits and demerits appreciated. It is gratifying to see the French text with formulas in which the exponents are inferiors, but then this is a Belgian book, and Belgian chemists are in accord it seems with their brethren in other countries except France. The mechanical execution of the book is commendable, but the most extraordinary feature is the enormous number of typographic errors. This is all the more startling when it is remembered that these volumes are a third printing and much of the matter was probably set up from type. The inorganic section contains four closely printed pages of errors and the organic section three and one-half pages. The error modulus goes further, for not only are there errors in the text which are not indicated in the errata list, but these lists contain errors. The organic list is headed "erratum," and in the inorganic list a limited checking has shown two errors. Page 2 should be page 12, and further on line 1 should be line 8. In the table of elements on page 69, the symbol for gadolinum is given as Ga and the symbol for boron is given as Bo, but this latter is evidently a deliberate change, as the same symbol is used in the section on boron and in the formula of boron compounds. It is very strange that a professor in a great university should mutilate the table of symbols in this manner. The same criticism applies to the

spelling "crypton," instead of "krypton" in this table. Curiously enough, the name is given as "krypton" in the section in which the argon group is described, although the author promptly falls from grace using the wrong spelling in the rest of the paragraph. It seems inexplicable that an intelligent chemist could be guilty of such irregularity.

Taken all in all it seems to the reviewer that notwithstanding the large amount of information in this work and attention that has been given to the modern phases of the science, the gross carelessness in the proof reading must render it an unsafe guide to the student. With a careful revision by a competent proof reader, the book would be made into an excellent manual of chemistry.

HENRY LEFFMANN.

THE FEDERAL POWER COMMISSION: ITS HISTORY, ACTIVITIES AND ORGANIZATION. By Milton Conover. 8vo, 117 pages, bibliography and index. The Johns Hopkins Press, Baltimore. \$1 net.

THE WEATHER BUREAU: ITS HISTORY, ACTIVITIES AND ORGANIZATION. By Gustavus A. Weber. 8vo, 70 pages, bibliography and index. Same publisher. \$1 net.

The two books are issued by the Johns Hopkins Press on behalf of the Institute for Government Research, which is an association of citizens coöperating with public officials in the scientific study of government with a view to promoting efficiency and economy in public affairs. With this purpose, close and intimate studies are made of the several departments, and in the volumes before us two very important departments are discussed.

The Weather Bureau is very well known to the people of the United States. Its great services to farmer, mariner and shipper are appreciated, though the forecasters come in not infrequently for both serious and flippant criticism. There are now in the United States over 6000 meteorological stations, and it is estimated that over thirty thousand are established in the world. Systematic weather observations were undertaken in the United States in 1870, in connection with the Signal Service, but in 1891, the bureau was transferred to the Department of Agriculture. It is stated that the earliest regularly organized observations were inaugurated by the Duke of Tuscany in 1654. The operation lasted about thirteen years. The publication of forecasts began in the United States on February 19, 1871, being called "probabilities" and the officer in charge of these was dubbed by the newspapers "Old Probabilities." The text of the book covers a large amount of information on the organization and work of the Weather Bureau.

A volume is devoted to the work of Federal Power Commission, which is composed of the Secretaries of War, Interior and Agriculture, having been created in 1920, to exercise a broad administrative function over water-power sites located on the navigable waters, public lands and reservation of the Nation. The extent of the water-power resources of the country, the steady growth of utilization thereof, and the activity of inventors in devising apparatus for such utilization, make the functions of the commission very important. The United States is probably somewhat backward in realizing on its water-power reserves. Foreign engineers have developed this source very extensively. "White coal" is widely used in many European countries. It is estimated that

there is sufficient water-power in the United States to do the work of 500,000,000 tons of coal annually. It is interesting to speculate what advantage would result if any considerable proportion of this substitution could be made. The coal question would be practically eliminated and the smoke nuisance in great part disappear. One of the most important phases of the water-power question is the linking up of the more powerful stations in such a way that power can be distributed over large areas. Surplus stations could be established to take the place of stations temporarily disabled, and also stations at which the supply of power is somewhat intermittent could be erected. In early days the water-driven mill was one of the most familiar objects in the settled area, but the material to be manufactured had to be brought to it and as it was usually located in a somewhat hilly country, the transportations were slow and expensive. Now the water-power machinery may be located in a mountainous region almost inaccessible to ordinary wagons or railroads, as the power can be transmitted with little loss many miles to the most convenient points. The book will be of great interest to industrial chemists and power engineers.

HENRY LEFFMANN.

METALS AND THEIR ALLOYS. A modern practical work dealing with metals from their origin to their useful application—both individually and as parts of alloys—used where strength, ductility, toughness, lightness, color, hardness, cheapness, conductivity, or bearing properties are demanded. By Charles Vickers. Partly based on the third edition of "Metallic Alloys" by William T. Brannt. 767 pages, illustrations, 8vo. New York, Henry Carey Baird and Company, Inc., 1923. Price \$7.50.

For many years in the non-ferrous foundry industry, the work of the late William T. Brannt, "Metallic Alloys," has been used as a reference book. It has now been some years since a new edition of Brannt has been published. Vickers recognized the desirability of a thorough revision of Brannt's work and proceeded with that end in view. So numerous were the additions and so completely did the older work require revision, that instead of revising Brannt's work, he has in reality given to the foundry a new work. Mr. Vickers writes from the standpoint of a practical foundryman, being a specialist in melting, alloying and casting metals. He has for a number of years been a technical editor on trade papers connected with the non-ferrous foundry industry.

The first chapter is devoted to a discussion of the elements; the second to a history, production, methods, properties and uses of the elements; the third chapter to alloys, historical, fundamentals, definitions, groups; chapter 4, characteristics of alloys; chapter 5, the art of alloying: melting and combinations. In the following chapters up to chapter 28, he deals with alloys of the common metals. Chapter 28, surface coloring of alloys; chapter 29, foundry utilization of scrap metals; chapter 30, analysis of babbitt metals; chapter 31, foundry data.

The work is considered one of reliability and of good practical value to the foundryman and the manufacturer of alloys.

G. H. CLAMER.

STATISTICAL BIBLIOGRAPHY IN RELATION TO THE GROWTH OF MODERN CIVILIZATION. By E. Wyndham Hulme, B.A., Sandars Reader in Bibliography, Sometime Librarian of the Patent Office. Printed for the author by Butler and Tanner. Grafton and Company, London. Small 4to, 44 pages, tables and charts.

This book contains the substance of two lectures delivered at the University of Cambridge in 1921. It represents an unusual line of investigation. It is an effort to determine what may be called the "moment" of civilization at a given date by an analysis of the bibliography thereof. The inquiry is limited to England, undoubtedly due to the vastness of the subject and to the especial opportunities which the author had through his professional positions. Yet it would seem that the attempt to write the history of civilization by examining British records would be somewhat like attempting to build up a department of natural history by examining the rocks, fauna or flora of limited area. This is not said in derogation of the book, for the ideas upon which it is based are original and the data given are evidently derived by careful and difficult searching. The author, indeed, is conscious of the partial character of the work, and makes special mention of the data that German libraries are said to contain, such as a large collection of works on pyrotechnics, the term being used in a wide sense, and not in our ordinary limit of "fireworks." There is, however, another point to be regarded. How far has the destruction of manuscript affected the record of human literary and scientific activity? The mistake of taking existing material as indexes of the character of a given age has been frequently made in geology and anthropology. Darwin's chapter on the imperfection of the geological record has a value beyond the purpose for which it was written. It is a trite remark that we cannot know the extent of our ignorance, but it is a principle that is often overlooked. Mr. Hulme is an evolutionist. He evidently regards that doctrine as no longer in dispute. He does not expect any radical change in the human race. "Man," he says "represents a type of organism in its approximately final stage." Neither in his mental nor physical structure "has he visibly advanced or receded from the standard to which he is found to conform in the paleolithic age." This is somewhat discouraging, and many biologists and sociologists may take issue with the assertion. Our knowledge of prehistoric man is very scanty. In some periods he evidently had considerable artistic ability, both in painting and sculpture, but this work was almost entirely reproductions of objects with which he was familiar. Of the dramatic, inventive side of art there is little if any record. Yet as regards the *historic* human being, at least, not further back than a few milleniums, it may be said that while the race has gained enormously in knowledge, it has not gained much in wisdom. The basic principles of human action were as familiar to the ancient Egyptians, Babylonians, Jews and Greeks as to us. Our notions of the life and work of these peoples are unquestionably seriously restricted by the lack of a large amount of literature that has been destroyed.

Necessarily, the extent of the book enables the author to give only a limited survey of his subject. A list is given of the manuscripts preserved in the British Isles dating not later than 1500. It appears that medical treatises constitute

half of the items of this list, while the art of war, architecture and decorative arts are represented by very few titles. Taken as an index of human activities during that period, it seems to show that by far the most energy was given to healing. Undoubtedly, disease is always with us, and always such as to urge us to secure relief, but the period covered by the list was a period of war, building of castles and churches, and development of many forms of decoration.

As an index of the character and extent of British progress in the applied arts and sciences, a list of British patents from 1561 to 1921 is given in a graph, with comparative population curves. There seems to be a typographic error on page 19, since the chart is there stated to give the patents from 1550 to 1821. In the copy in hand there has also been, apparently, a mis-binding of charts, as No. 3 immediately follows No. 1.

A graph is also given of population-increase and issue of patents in the United States from 1850 to 1921. The lines follow pretty closely. There is a distinct peak from 1914 to 1918, which may be in part due to the stimulation in invention in war appliances on account of the extensive introduction of new methods of offence.

A curious fact is mentioned in connection with the beginning of the literature of Technology. "The order of the appearance of this literature is not the order of utility, for the literature of Technology begins with Song, or as we should call it to-day—Didactic Poetry." The reference is to a poem, "Dyer's Fleece," which describes a spinning invention of Lewis Paul a year before it was patented. The author's outlook on the present-day industrial civilization is that "the Age of Power is approaching its natural limits." "Thus, the industrial future of civilization must be in the direction of a gradual transformation of its mineral basis to one founded upon the utilization of natural sources of energy and the building up of products from elements of which there is practically an inexhaustible supply."

The book contains a large amount of original and interesting matter, well worth the attention of the sociologist and historian. The author deserves much credit for the labor he has bestowed on the text, tables and charts, by the preparation of which he has opened a new and useful field of discussion. Necessarily, some of the statements will arouse dissent, and the data presented constitute but a small proportion of what will be needed for definite conclusions.

HENRY LEFFMANN.

REPRINT AND CIRCULAR SERIES OF THE NATIONAL RESEARCH COUNCIL. Fine and Research Chemicals, second revision. Issued by the Committee on Research Chemicals, Clarence J. West, Secretary of the Committee. 45 pages, 8vo, pamphlet. Washington, District of Columbia, Council, 1923.

This list of several thousand rarer chemicals, now made in the United States, is an encouraging indication of the degree to which this country is becoming independent of other nations, especially Germany. A list of firms engaged to a greater or less degree in such manufacture is given, and such firms as sell directly in comparatively small lots are noted, which will be of much use to the ordinary worker. It is reported that biological stains and indicators, which have for a long while been regarded as special German

products, are now made in the United States of fully satisfactory quality. Several of the national societies, of which the members are specially interested in these stains, have joined in forming a committee which will begin very shortly issuing certificates for each stain, which will be marketed with a label stating the accuracy of the sample.

HENRY LEFFMANN.

THE BEVERAGE BLUE-BOOK FOR 1923. 334 pages, 8vo. H. S. Rich and Company, Chicago, 1923.

This is the annual standard directory, buyers' guide and reference volume for the beverage industry of the United States, covering the class commonly termed "soft drinks." This has been for many years a very active business in this country, and since the establishment of prohibition legislation it has greatly increased. Material improvement has taken place on all the details of the manufacture, especially by the introduction of liquefied carbon dioxide. The book contains not only a list of the manufacturers and bottlers of these beverages, of which there is a great variety of types, but some text of special interest to those engaged in the business. Many illustrated and display advertisements show how mechanical ingenuity has been encouraged in connection with the bottling and marketing of the beverages.

HENRY LEFFMANN.

WOOD DISTILLATION. By L. F. Hawley, in charge of section of Derived Products, Forest Products Laboratory. 136 pages, 28 illustrations, 8vo. The Chemical Catalog Company, New York, 1923. Price \$3 net.

This is one of the American Chemical Society's Monographs, and in general form and character follows the preceding volumes. It appears from the preface that books in English on wood distillation are few in number and in some cases not of high value. Two works in foreign languages are mentioned as excellent. One is German; the other Swedish. It is much to be regretted that the secondary languages of western Europe are so often used for the medium of valuable scientific data. Of the Scandanavian tongues, Swedish is probably the most difficult. Books written by foreign authorities are always more or less misleading to American workers, and, therefore, the present work, which is the result of large experience and much research in our own operations, will be welcome to American chemists. In colonial days, forests were extensive and trees large. Great waste occurred by the manufacture of charcoal for the iron furnaces, and extensive areas were denuded. In other regions, especially in the Blue Mountains, much deforestation occurred by the cutting of hemlock spruce for the bark, which was used for tanning. In the early manufacture of charcoal, the by-products were not collected, but a distillation industry has developed on account of the demand for certain ingredients of the condensable vapors. Among these are acetic acid, methyl alcohol and acetone. Special woods, such as beech, give a tar containing kreasote. Methyl alcohol was long used as a substitute for ethyl alcohol in many industrial processes, and was, unfortunately, also used in medicinal preparations and beverages, being much cheaper, when the tax was paid on the latter. It is probable that methyl alcohol could not compete with pure, untaxed ethyl alcohol.

Much improvement has taken place in the wood distillation machinery of late years. The demand for crude methyl alcohol as a denaturing material, and the wide market for calcium acetate and charcoal have given impetus to the industry.

The work is in two parts. Destructive distillation of hard woods occupies eighty-two pages, the remainder being devoted to the distillation of resinous woods. A recent and promising development of the procedures is the distillation of sawdust and chips. These materials have several advantages over larger masses. They can be more rapidly and thoroughly dried, are cheaper and can be applied in a continuous process. They are, however, not without some disadvantages which special mechanical methods are necessary to overcome. Wood is a poor conductor of heat, and sawdust is, of course, still poorer. A stirrer or a rotating retort is needed, and the finely divided charcoal is difficult to cool when in large amount, indeed, may be the cause of serious explosions. One company has, however, avoided these disadvantages to a certain extent, by bricketting the sawdust. If heavy pressure is used, a solid mass can be formed without any binding material. Other methods have been devised, which are described in detail. The tar of hard wood distillation has had, as yet, but limited application, although its use is increasing. A special ingredient of beech tar, kreasote, is now prepared in the United States.

Tables of analyses of many woods are given. The data show the progress that has been made in the detection and determination of the more or less complicated proximate principles occurring in vegetable structures. It appears, however, from occasional statements in the text that many data both as to the composition of the raw materials and of the products, as well as details of procedures, remain to be ascertained. In connection with the production of charcoal, attention may be called to the interesting data obtained during the war concerning the conditions under which it acts as an adsorber of gases. This phase of the subject is not within the scope of the work, and is, therefore, not discussed. Information is given as to the refining of the more important volatile products of the distillation.

The second part of the book is devoted to the methods and results of distillation of resinous woods. Two distinct systems are here applied: Destructive distillation and with steam. The methods and apparatus employed in the first form are somewhat various in type. On account of the resinous ingredients, the tar produced floats on the watery portion which contains the pyroligneous acid. The latter is usually a waste product, the valuable ingredients being in the tar, from which volatile oils of the turpentine class are derived. Steam distillation has the advantage that much smaller pieces of wood may be used. Turpentine and rosin are the most valuable products of this procedure. The yields are of better quality than those of the destructive distillation. One product, steam distilled pine oil, comparatively new to the market, was at first not well received, but is now finding many applications.

The book is filled with important and interesting information, and not the least value of it are the indications that it offers for research in the line of industrial applications of wood products.

HENRY LEFFMANN.

THÉORIE DES NOMBRES. Par M. Kraitchik, Ingénieur à la Société Financière des Transports et d'Entreprises industrielle, Directeur à l'Institut des Hautes Études de Belgique avec une préface de M. d'Ocagne. ix + 229 pages, $6\frac{1}{2}'' \times 9\frac{1}{2}''$. Paris, Gauthier-Villars et Cie., 1922. Price, in paper, 25 Francs.

The present work is an account of the elements of the theory of numbers and constitutes an introduction to the further development of the theory. It is the intention of the author in succeeding volumes to prosecute derived theories, but as far as the subject is covered, even this first volume will render valuable service to all who are interested in the various investigations of numbers.

Mr. Kraitchik's contribution to the subject is to have conceived the most reliable, the easiest and quickest methods possible of "sieving" or elimination processes upon groups of numbers of such magnitude as to discourage the application of all usual tentative methods. Whereas the usual "sieving" processes could scarcely be practically applied to more than thirty or forty possible values, that of Mr. Kraitchik permits, with no greater expenditure of labor or time, the application of the operation to groups comprising several millions and even several tens of millions of numbers, without which, thanks to an effective graphic plan, it would be necessary to write out those numbers. Mr. Kraitchik has gone even further; he has outlined the elements of a mechanism by the aid of which the process of "sieving" may be effected by the use of a special calculating machine.

LES APPLICATIONS ÉLÉMENTAIRES DES FONCTIONS HYPERBOLIQUES À LA SCIENCE DE L'INGÉNIEUR ÉLECTRICIEN. Par A. E. Kennelly, Professeur d'Électricité appliquée, Université de Harvard, Directeur des Recherches électriques appliquées, Massachusetts Institute of Technology, Professeur américain d'Échange auprès des Universités françaises 1921-22. viii-153 pages, $6\frac{1}{2}'' \times 9\frac{1}{2}''$ inches, paper. Paris, Gauthier-Villars et Cie., 1922. Price, 15 Francs.

There is undoubtedly greater inclination in Continental Europe to translate into the language of the country important technical works than exists in English-speaking countries, and the lack of English translations of certain important foreign technical works has been often a matter of comment.

At the first glance upon the title and authorship of this work with the make-up of the familiar cover-page of its noted publishers, the first impression is that with their usual appreciation of technical merit, they have issued a translation of the distinguished author's account of his highly original mathematical devices which eliminate so much of the labor entailed in alternating current transmission lines. Upon a closer view, it is not a mere translation, but a distinct work in French by Doctor Kennelly himself.

During the scholastic year 1921-1922, Doctor Kennelly was among the leading scientists chosen to represent seven eastern universities in the exchange professorship movement. In issuing his lectures in the language of the country in which they were delivered, the author has adopted a graceful means of acknowledging the appreciation and cordial reception of his French auditors.

LA COMPOSITION DE MATHÉMATIQUES DANS L'EXAMEN D'ADMISSION À L'ÉCOLE POLYTECHNIQUE DE 1901 À 1921. Par F. Michel, Ancien élève de l'École Polytechnique, Licencié ès Sciences Mathématiques, Ingénieur Chef des Services électriques du Chemin de fer du Nord, et M. Potron, Ancien élève de l'École Polytechnique, Docteur ès Sciences Mathématiques. xii-452 pages, $6\frac{1}{2}'' \times 9\frac{1}{2}''$. Paris, Gauthier-Villars et Cie., 1922. Price, in paper, 40 Francs.

In publishing this new collection of problems in mathematics given in the competition, examinations for entrance to the École Polytechnique for 1901 to 1920, the authors warn the user not to expect from their study a panacea for passing a successful examination. Nevertheless, there is profit as well as comfort for a prospective candidate to be derived from a set of such papers, covering a term of years, with solutions to the problems.

The object of this examination is not alone to test the students' knowledge of fundamental processes, but also his ability to apply them, a point of great importance in determining mathematical aptitude. The mode of attack is indeed only second in importance to thorough grounding in mathematical processes and dexterity in algebraic transformation. With that object, the questions, more often than not, are presented without regard to classification of the processes which are to be employed in their solution. Further, another question is often derived from a preceding one, and book-rote is replaced by a test of professional capacity.

The work is in two separate parts. The first part consists of the examination questions with their solution and explanation. In the second part, in the order in which the various topics of the course have been presented, specific problems occurring in the first part are discussed. The scope of the subject matter is substantially similar to that offered in the science courses in American universities. These entrance requirements cover what in this country is required for post-graduate study in this subject. When it is considered that the two years' course at the École Polytechnique is prerequisite to entrance, to such special professional schools as the École Nationale Supérieure des Mines or the École des Ponts et Chaussées, it is evident that a high order of scholarship is expected in professional study "over there."

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 158, Mathematical Equations for Heat Conduction in the Fins of Air-cooled Engines. By D. R. Harper, 3rd, and W. B. Brown. 32 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This report deals with the problem of reducing actual geometrical area of fin-cooling surface, which is, of course, not uniform in temperature, to equivalent "cooling" area at one definite temperature, namely, that prevailing on the cylinder wall at the point of attachment of the fin. This makes it possible to treat all the cooling surface as if it were part of the cylinder wall and 100 per cent. effective.

The quantities involved in the equations are the geometrical dimensions of the fin, thermal conductivity of the material composing it, and the coefficient of surface heat dissipation between the fin and the air stream. Several assumptions of a physical nature are thus necessarily involved in making the

problem possible of solution. These are set forth in detail, and the limitations which result from them in applying the equations to numerical calculation are carefully pointed out.

An expression for approximate fin effectiveness is developed, based upon simple mathematics and very convenient in form for engineering use. The essence of the paper is an examination into the magnitude of the errors involved in using this expression without correction and a determination of the corrections needed for accurate work. The mathematical expressions involved are quite complicated, including Fourier's series, super-Fourier's series, Bessel functions of zero order of two kinds with imaginary arguments, etc. The results of the work are collected in graphical form in a series of charts, so that the design engineer can use the simple formula first developed and apply to it corrections readily read from the charts, thus avoiding entirely all higher mathematics.

Report No. 159, Jet Propulsion for Airplanes. By Edgar Buckingham. 18 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This report is a description of a method of propelling airplanes by the reaction of jet propulsion.

Air is compressed and mixed with fuel in a combustion chamber, where the mixture burns at constant pressure. The combustion products issue through a nozzle, and the reaction of the jet constitutes the thrust.

Data are available for an approximate comparison of the performance of such a device with that of the motor-driven air screw. The computations are outlined and the results given by tables and curves.

The relative fuel consumption and weight of machinery for the jet decrease as the flying speed increases; but at 250 miles per hour the jet would still take about four times as much fuel per thrust horsepower-hour as the air screw, and the power plant would be heavier and much more complicated.

Propulsion by the reaction of a simple jet cannot compete, in any respect, with air screw propulsion at such flying speeds as are now in prospect.

Report No. 162, Complete Study of the Longitudinal Oscillation of a VE-7 Airplane. By F. H. Norton and W. G. Brown. Five pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This investigation was carried out by the National Advisory Committee for Aeronautics at Langley Field in order to study as closely as possible the behavior of an airplane when it was making a longitudinal oscillation. The air speed, the altitude, the angle with the horizontal and the angle of attack were all recorded simultaneously and the resulting curves plotted to the same time scale. The results show that all curves are very close to damped sine curves, with the curves for height and angle of attack in phase, that for angle with the horizon leading them by 18 per cent. and that for the path angle leading them by 25 per cent.

Report No. 164, The Inertia Coefficients of an Airship in a Frictionless Fluid. By H. Bateman. 16 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

Report No. 164 deals with the investigation of the apparent inertia of an airship hull. The exact solution of the aerodynamical problem has been studied

for hulls of various shapes and special attention has been given to the case of ellipsoidal hull. In order that the results for this last case may be readily adapted to other cases, they are expressed in terms of the area and perimeter of the largest cross-section perpendicular to the direction of motion by means of a formula involving a coefficient K which varies only slowly when the shape of the hull is changed, being 0.637 for a circular or elliptic disc, 0.5 for a sphere, and about 0.25 for a spheroid of fineness ratio 7. For rough purposes it is sufficient to employ the coefficients, originally found for ellipsoids, for hulls otherwise shaped. When more exact values of the inertia are needed, estimates may be based on a study of the way in which K varies with different characteristics and for such a study the new coefficient possesses some advantages over one which is defined with reference to the volume of fluid displaced.

The case of rotation of an airship hull has been investigated also and a coefficient has been defined with the same advantages as the corresponding coefficient for rectilinear motion.

Report No. 167, The Measurement of the Damping in Roll on a JN4h in Flight. By F. H. Norton. 6 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This investigation was carried out by the Committee for the purpose of measuring the value of L_p in flight. The method consisted in flying with heavy weights on each wing tip, suddenly releasing one of them, and allowing the airplane to roll up to 90° with controls held in neutral while a record was being taken of the air speed, and angular velocity about the X-axis. The results are of interest as they show that the damping found in the wind-tunnel by the method of small oscillations is in general 40 per cent. higher than the damping in flight. At 50 m.p.h. the flight curve of L_p has a high peak, which is not indicated in the model results. It is also shown that at this speed the lateral manœuverability is low.

U. S. COAST AND GEODETIC SURVEY. Terrestrial Magnetism. Horizontal Intensity Variometers. By George Hartnell (Special Publication No. 89). Sixty-two pages, illustrations, plate, 8vo. Washington, Government Printing Office, 1922. Price, 10 cents.

A variometer is an instrument containing a suspended or supported magnet which is free to move under the action of a varying magnetic field. The magnet is placed at right angles to that particular component of the field which is being investigated. Magnetic observatories are equipped with a set of three variometers collectively called a magnetograph. The D variometer indicates changes in *declination*. The Z variometer indicates changes in the *vertical intensity*. The theory of the Z variometer was discussed in the *Journal of Terrestrial Magnetism and Atmospheric Electricity*, June, 1919.

This publication treats of the characteristics of the third variometer of the magnetograph, namely, the *horizontal intensity variometer*. The paper is divided into two parts. Part I deals with the theory of the horizontal intensity variometer proper, and discusses in considerable detail the characteristics of the bifilar and unifilar variometers, and also characteristics common to both.

Part II is a study of the two types of suspension. As an indication of the nature of the discussion, one characteristic is selected for special mention.

The magnet suspended by a quartz fibre under torsion is unequally deflected and the field is increased and decreased by equal amounts, consequently the horizontal intensity variometer in which the magnet is held perpendicular to the field by the torsion in the fibre is less sensitive when the field increases than when it decreases, that is, the scale value is greater for ordinates indicating a larger field intensity. The inequality is so large in unifilar quartz suspensions as to necessitate a correction to the variometer. Its magnitude is determined by the coefficients in a series of developments of the scale value in powers of the ordinates. It is shown how this inequality in scale value can be eliminated and a constant uniform scale value secured by means of a fibre of suitable size and a control magnet to reduce the scale value to the desired amount.

The publication treats the subject of horizontal intensity variometers in a comprehensive manner and will prove of value to those operating or designing these instruments.

PUBLICATIONS RECEIVED.

Statistical Bibliography in Relation to the Growth of Modern Civilization. Two lectures delivered in the University of Cambridge in May, 1922, by E. Wyndham Hulme, B.A., Sandars Reader in Bibliography, Sometime Librarian of the Patent Office. 44 pages, tables, charts, quarto. London, printed for the author by Butler and Tanner, 1923.

Wood Distillation, by L. F. Hawley. American Chemical Society Monograph Series. 141 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1923. Price \$3.

Mirrors, Prisms and Lenses. A textbook of geometrical optics by James P. C. Southall. Enlarged and revised edition. 657 pages, illustrations, 12mo. New York, The Macmillan Company, 1923.

The Beverage Blue Book, 1923. The Standard Directory, Buyers' Guide and Reference Volume for the Beverage Industry. 324 pages, illustrations, 8vo. Chicago, H. S. Rich and Company, 1923.

National Advisory Committee for Aeronautics: Technical Notes No. 149, Influences in the Selection of a Cycle for Small High-speed Engines Running on Solid or Airless Injection with Compression Ignition, by Robertson Matthews. 11 pages, illustrations, quarto. Washington, District of Columbia, Committee, July, 1923.

Animal-eating Plants. HEBER W. YOUNGKEN, of the Philadelphia College of Pharmacy and Science (*Amer. Jour Pharm.*, 1923, xcv, 329-350), states that approximately 500 species of green plants are carnivorous or animal-eating. Their leaves have become modified to allure, capture, imprison, digest and absorb their prey. The chief carnivorous plants are the sun-dews, fly-traps, pitcher-plants, bladder-worts, and butterworts.

J. S. H.

CURRENT TOPICS.

The Reaction Consequent upon the Evaporation of a Liquid and upon the Emission of Vapors from Small Orifices. W. G. DUFFIELD. (*Phil. Mag.*, April, 1923.)—The original problem which the author set out to solve was “whether in the process of evaporation or boiling into the open air, there were any measurable mechanical reaction upon the surface from which the molecules were issuing.” Ether in a covered crystallizing dish was put on the pan of a balance and equipoised. Upon the removal of the cover the liquid began to evaporate but no downward recoil of the liquid due to the projection of molecules upward manifested itself. From the rate of evaporation and the normal velocity of molecules of ether vapor at the temperature of the experiment this recoil should have amounted to .054 gram weight, but it did not exist. Later, on a balance pan 3.20 gms. water were boiled away in 20 secs. Theory would indicate that the consequent downward thrust should amount to 11.4 grs., a weight equal to several times that of the water. The pan with the water should not have risen, but as a matter of fact it did, owing to the disappearance of the water. Manifestly there is something wrong with the theory, for the force of recoil could have been detected had it been even one-hundredth as great as it was computed to be. “Is it absent because the general view is wrong that the molecules issue with the velocity we have assigned to them; do they instead of being projected like bullets just drop off? Do they suffer so much in velocity in penetrating the surface layer?” An experiment was made which showed that the recoil exists and manifests itself when evaporation takes place, not into air or other gas or vapor, but into a vacuum. This goes to prove that the molecules start away from the liquid with high velocities and that in some manner it is the presence of the gas or vapor above which causes the looked-for reaction to fail to appear. “There is some compensating interaction between the projected molecules and the molecules of air or previously evaporated material in the space above the liquid, which prevents the loss of momentum of the projected material from becoming evident as a pressure upon the surface.” To clarify the problem the author proposes an analogy. Let there be a gun platform carrying a thousand cannon each shooting a ball in the same horizontal direction once a second. The reaction on the platform would be the same, no matter whether the balls went into a near-by sand bank or passed out of sight. This represents the case without complications. Any evaporating liquid not in vacuo has beating on its surface a procession of molecules from the space above it. “It is as though our gun platform were being bombarded by enemy fire, which we can picture as occasioning a pressure which might be measured by the com-

pression of a spring. Upon our opening fire, there is an additional reaction if our cannon balls do not strike those of the enemy (*i.e.*, if the cannon ball density is low), but if they do collide in such a way that each ball stops or diverts an enemy ball, the reading of the sprig will remain unaffected by the discharge of our guns, since each discharge both contributes a certain amount of kick to the platform and robs it of the impact of an enemy shell. But it is not infinitely probable that each enemy shell will meet one of ours in such a way as to be prevented from delivering its momentum to the platform, so that the neutralization is not likely to be complete unless the discharge rate is very great," that is, unless the enemy fire is heavier than ours, so that each of our shots shall meet a hostile ball. If we want to notice the recoil, our fire must exceed that of the enemy so that many of our balls shall get away without having struck an oncoming projectile. And this is later shown to be true in the case of jets of steam.

Let him who thinks himself well informed in matters of evaporation and boiling read this paper that he may recognize his ignorance.
G. F. S.

The True Oil-bearing Milkweeds.—Note was made in a recent issue of this JOURNAL of the extraction of oil from the seeds of several species of *Asclepias*, commonly known as milkweeds. The note was based on an article in the *Bull. d. Mat. Gras.* of Marseilles. It appears that the editor of that publication was misled by the term milkweed, and that the plant from which the oil is obtained is the Mexican poppy, *Argemone mexicana*. This is a member of the Papaveraceæ, the family to which the opium plant and the now famous Flanders poppy belong. Many of the plants of this group have a milky juice, so that they may be called milkweeds in some localities. In some species, however, the juice is highly colored, as in the common celandine. The account given by the French journal was probably taken from Spanish sources. An abstract in English is given in the initial number of the new series of the *International Review of Science and Practice of Agriculture*, p. 216. The constants of the oil are given in detail.
H. L.

First Annual Report of the International Committee on Chemical Elements.—For a number of years an international committee on atomic weights was engaged in compiling data concerning revisions of atomic weight determinations, publishing annually a table of approved figures. This committee was appointed by the International Association of Chemical Societies, which was broken up by the war, and the operations of its committees temporarily suspended. After the war closed, the representatives of several of the nations that had been allied against the Central Powers formed the International Union of Pure and Applied Chemistry, which created a committee designated as the International Committee on Chemical Ele-

ments. The change of title and scope is rendered necessary by the great progress in the field of isotopy, first recognized in connection with the radioactive elements, but now extended to many other groups. The duty of the committee will be to keep chemists informed of the progress of discovery in this promising field. It consists at present of eight members representing United States, Great Britain, France and Czecho-Slovakia. Germany and Austria have not yet been taken into the fold. In addition to constituent members the committee has special experts and two honorary presidents.

Under these auspices a first report has been issued containing tables of isotopes and radioactive elements. The committee considers that its work in this field is only provisional. Recognizing that the definitions and nomenclatures adopted are not homogeneous, the committee regards some changes as necessary, but, pending general approval, has made only a few modifications and has deemed it proper to submit these to the judgment of the discoverers. The names "radon," "actinon," and "thoron" were, therefore, submitted to Rutherford and Curie, and as these names are given in the tables, it is presumed that they have been approved.

The following definitions are taken from the report:

A chemical element is defined by its atomic number. This number represents the excess of positive over negative charges in the constitution of the atomic nucleus. Theoretically, the atomic number also represents the number of electrons which rotate around the central positive nucleus of the atom. Each atomic number represents the place occupied by the element in the Mendeleef table. If the above definition is accepted, elements may be simple or complex, according as their atoms are all of the same mass or not. Complex elements consist of as many isotopes as its atoms have different masses, therefore, consist of a mixture of isotopes. All elements considered as units are represented by their standard symbol, but to represent isotopes, the symbol is modified by an exponent indicating the mass of the given isotopes. In the English text, this exponent is written as a superior, for example, Cl^{35} refers to the chlorine isotope having the atomic mass of 35. In the French text (the report is bilingual) the isotope is represented by Cl_{35} . This is probably due to the fact that French chemists use the old form of exponent, written as a superior and, therefore, just reverse the methods followed by all other nations, but this practice is slowly disappearing and it is to be hoped that uniformity may be soon attained. In establishing the mass of the isotope, oxygen is, as usual, taken as 16. The isotopes of lead which are the ultimate result of disintegration of radioactive elements and the radioactive isotopes will alone appear in the international table of radioactive elements. The expression "atomic mass" is reserved for isotopes or simple elements considered from the isotopic point of view. The expression "atomic weight" retains its usual meaning, and is applied to elements without consideration of their isotopic constitution.

The pamphlet contains a table of over thirty elements, mostly the abundant ones, with several data, among which the most interesting is the statement of the number of isotopes so far elucidated. Lithium is the element of lowest atomic weight that is given as having isotopes, consisting of two with respective masses of 6 and 7. Boron has two, respectively, 10 and 11. Silicon is given two (28 and 29) with provisionally a third (30). Selenium is given six and tin seven with a possible eighth. Xenon is given seven with possibly two more. A large table is appended, giving the three series of radioactive elements, *viz.*, uranium-radium series, ending with radium \mathcal{Q}' which is isotopic lead, the actinium series and the series of thorium, which last also ends with lead (Th \mathcal{Q}'), but the lead terminating the radium series has a different atomic mass (that is, is a different isotope) from that ending the thorium series, the former being Pb^{206} , the latter Pb^{208} .

An inspection of the table will show the extraordinary development that has taken place in the knowledge of the nature and properties of the chemical elements.

H. L.

The Ionization of Potassium Vapor by Light. R. C. WILLIAMSON. (*Phys. Rev.*, Feb., 1923.)—"Experimental results relative to the ionization of metallic vapors by light have been very meagre, and it is difficult to point to any phenomena which are due, without doubt, to ionization by radiation of optical frequencies." In this paper evidence from experiment is presented that potassium vapor is actually ionized by ultra-violet light. "This ionization begins with wave-lengths of about 3000 Å., and increases rapidly and continuously in amount as the wave-length of the exciting radiation decreases from 3000 to 1850 Å., the limits investigated. The number of atoms exposed for a second to a given intensity of radiation, per electron ejected from an atom, is of the same order of magnitude in the solid as in the vapor state, for wave-length regions corresponding to marked sensitivities in each case. For the intensities used in these experiments, this number was about 10^5 ."

G. F. S.



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PHYSICAL MEASUREMENTS OF AUDITION AND THEIR BEARING ON THE THEORY OF HEARING.*

BY

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THE question of how we hear has been a subject for discussion by scientists and philosophers for a long time. Practically every year during the past fifty years articles have appeared discussing the pros and cons of various theories of hearing. These discussions have been participated in by men from the various branches of science and particularly by the psychologists, physiologists, otologists, and physicists. During the past two or three years this discussion has been particularly acute. It is not uncommon to pick up an article and read in the beginning or concluding paragraphs statements such as the Helmholtz theory of audition seems to have sunk beyond recovery,^{90, 65} † and at the same time an article written probably a month later will have the conclusion that the Helmholtz theory of audition is definitely established beyond all controversy.⁷⁰⁻⁷⁵

There is apparently a great deal of misunderstanding between various writers because of different points of view due to different training. To the physicist it seems that most of the discus-

* Presented at the meeting of the Section of Physics and Chemistry of The Franklin Institute held Thursday, March 29, 1923.

† These numbers refer to the bibliography at the end of the paper.

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sions show a profound ignorance of the dynamics of the transmission of sound by the mechanism of the ear. Those discussions by the physicists are frequently open to criticism by the otologist and psychologist, due to his lack of knowledge of the structure of the ear or the mental reaction involved in the process of interpretation. I think it is fortunate that some of these scientists from the different branches are now coöperating in their research work as is evinced by the appearance of several joint papers. (Papers by Dean and Bunch, Minton and Wilson, Wegel and Fowler, Kranz and Pohlman, and others.)

It is not my purpose to discuss the merits of the various theories of hearing, but I desire to present some of the facts of audition which have been recently determined with considerable accuracy, and then discuss the theory of hearing which best explains these facts.

Hearing is one of the five senses. It is that sense that makes us aware of the presence of physical disturbances called sound waves. For my purpose, sounds may be classified into two groups, namely, pure tones and complex sounds. A pure tone is specified psychologically by two properties, namely, the pitch and the loudness. These sensory properties are directly related to the physical properties, frequency and intensity of vibration. Mixtures of pure tones of different loudness, but of the same pitch, fall under the first class, since such mixtures give rise to a pure tone. The complex sounds are varying mixtures of pure tones. It will be noticed that phase has not been taken into account. Except when using the two ears for locating the direction of sources of sound, phase differences are not ordinarily appreciated by the ear.*

These tones are usually transmitted by means of air waves through the outer ear canal to the drum of the ear. From here the vibrations are transmitted by means of the bones in the middle ear to the mechanism of the inner ear.

Those facts of audition which are familiar to almost everybody are as follows:

* This statement may require modification when more experimental data are available. As shown later in the paper the middle ear has a non-linear response. Consequently it would be expected that phase differences, especially between tones which are harmonic, would produce spacial differences in nerve stimulation.

1. Pure tones are sensed by the ear and differentiated by means of the properties *pitch* and *loudness*.

2. When two notes, separated by a musical interval, are sounded together, they are sensed as two separate notes. They would never be taken for a tone having the intermediate pitch. In this respect, hearing is radically different from seeing. When a red and a green light are mixed together, the impression received by the eye is that of yellow, an intermediate color between the two.

3. There is a definite limiting difference in pitch that can just be sensed.¹⁻⁹

4. There is a definite limiting difference in intensity that can just be sensed.¹⁰⁻¹⁴

5. There is a minimum intensity of sound below which there is no sensation.¹⁵⁻³¹

6. There is an upper limit on the pitch scale above which no auditory sensation is produced.³²⁻⁴⁴

7. There is a lower limit on the pitch scale below which there is no auditory sensation produced.⁴⁵⁻⁵¹

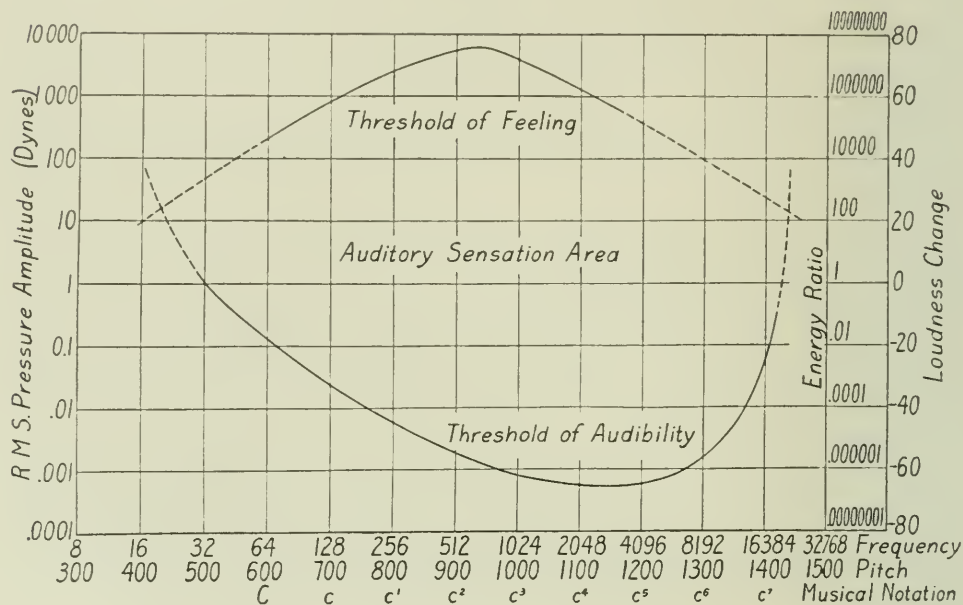
8. The ear perceives tones separated by an octave as being very similar sensations.

Another quality of audition which is not so commonly known was pointed out by A. M. Mayer.⁵² He stated that high tones can be completely masked by louder lower tones while intense higher tones cannot obliterate lower ones though the latter are very weak. Experiments to be described later in the paper show that this statement must be modified somewhat. Very intense low ones will produce a masking effect upon still lower tones, although the masking effect is very much more pronounced in the opposite case. Many of the opponents of the Helmholtz resonant theory of hearing claim that this fact is fatal to such a theory.⁵²

The new tools which have made possible more accurate measurements in audition are the vacuum tube, the thermal receiver and the condenser transmitter. When connected in a proper arrangement of circuits, the vacuum tube is capable of generating an oscillating electrical current of any desired frequency. This electrical vibration is translated into a sound vibration by means of the telephone receiver. Between the receiver and the oscillator, a wire network called an attenuator²⁸ is interposed which makes

it possible to regulate the volume of sound. The theory⁵⁴⁻⁵⁵ of the thermal receiver has been worked out so that it is possible to calculate its acoustic output from the electrical energy it is absorbing. In this way, it is possible to calculate the pressure variation produced in the outer ear canal when a tone is being perceived. A detailed description of the apparatus and method used in such measurements was given in a paper presented before the National Academy of Science, November 14, 1921.⁵⁵ Such

FIG. 1.



a combination of apparatus which has been calibrated is called an audiometer and is suitable for measuring abnormal as well as normal hearing. A receiver more rugged than the thermal may be substituted when its efficiency compared to the thermal receiver is known for all frequencies. By using such an audiometer, the average absolute sensitivity for approximately 100 ears which were considered to be normal was determined. The lower curve in Fig. 1, labelled the threshold of audibility, shows the results of such measurements. The ordinates give the amplitude of the pressure variation in dynes per square centimetre that is just sufficient to cause an auditory sensation and the abscissæ give the frequency of vibration of the tone being perceived. Both are plotted on a logarithmic scale. The experimental difficulties made it impossible to make a very accurate determination for

those parts of the curve shown by dotted lines. More work needs to be done on these portions of the curve. In the important speech range, namely, from 500 to 5000 cycles, it requires approximately .001 of a dyne pressure variation in the air to cause an auditory sensation. This corresponds to a fractional change of about one-billionth in the atmospheric pressure, which shows the extreme sensitiveness of the hearing mechanism.

In order to obtain an idea of the intensity range used in hearing, an attempt was also made to obtain an upper limit for audible intensities. When the intensity of a tone is continually increased, a value is reached where the ear experiences a tickling sensation. Experiments show that the intensity for this sensation is approximately the same for various individuals and the results can be duplicated as accurately as those for the minimum intensity value. It was found that if this same intensity of sound is impressed against the finger, it excites the tactile nerves. In other words, the sensation of feeling for the ear is practically the same as for other parts of the body. When the intensity goes slightly above this feeling point, pain is experienced. Consequently, this intensity for the threshold of feeling was considered to be the maximum intensity that could be used in any practical way for hearing. The two points where these two curves intersect have interesting interpretations. At these two points, the ear both hears and feels the tone. At frequencies above the upper intersecting point, the ear feels the sound before hearing it, and in general would experience pain before exciting the sensation of hearing. Consequently, the intersection point may be considered as the upper limit in pitch which can be sensed. In a similar way, the lower intersection point represents the lowest pitch that can be sensed.

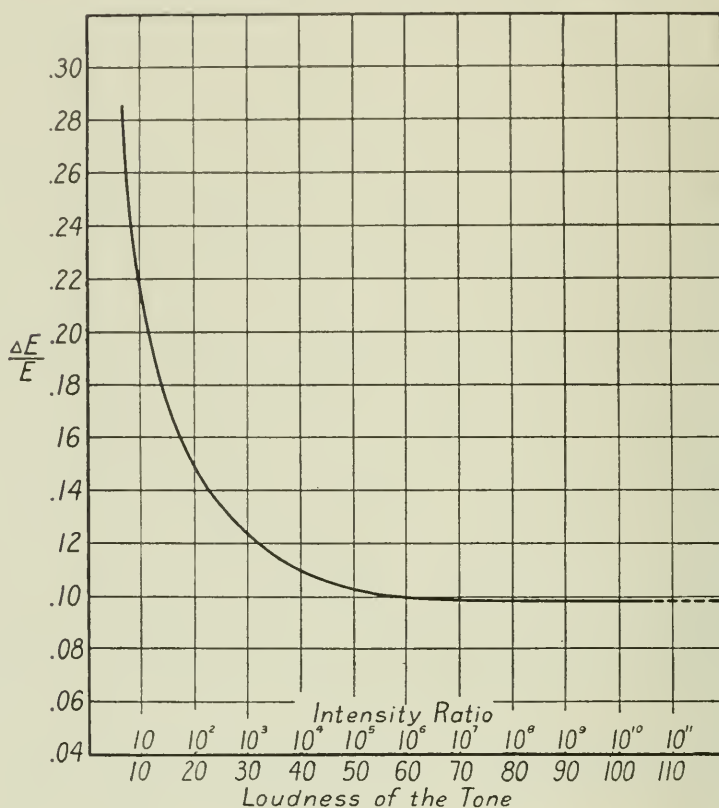
There has been considerable work³²⁻⁵¹ in the past to determine the upper frequency and lower frequency limits of audibility, but it would appear that without the criterion just mentioned, such limiting points apply only to the particular intensity used in the determination. Not enough attention has been paid to the intensity of the tones for such determinations. It is quite evident from this figure that both the upper and lower limits of audibility which are found in any particular experimental investigation will very largely depend upon the intensity of the tones sounded.

For example, if the intensity were along the .01 dyne line, the limits would be 200 and 12,600 cycles.

The area enclosed between the maximum and minimum audibility curves has been called the auditory-sensation area and each

FIG. 2.

Minimum Perceptible Difference in Intensity



point in it represents a pure tone. The question then arises: How many such pure tones can be sensed by the normal ear?

The answer to this question has been made possible by the recent work of Mr. V. O. Knudsen.¹⁴ In this work Knudsen made determinations of the sensibility of the ear for small differences in pitch and intensity. In Fig. 2, the average results of his measurements for changes in intensity are shown. Each ordinate gives the fractional change in the sound energy which is just perceptible, this fractional change being called the Fechner ratio. The abscissæ are equal to ten times the logarithm of the ratio of intensities, the zero corresponding to the intensity at the threshold of audibility. For intensities greater than 10^4 times the

threshold of audibility, the Fechner ratio has the constant value of approximately one-tenth. It was found that this ratio is approximately the same for all frequencies. In Fig. 3 is shown the results taken from Knudsen's article on the pitch sensibility. The ordinates give the fractional change in the frequency which is just perceptible and the abscissæ give the frequency on a logarithmic scale. The meaning of the pitch scale at the bottom of this

FIG. 3.

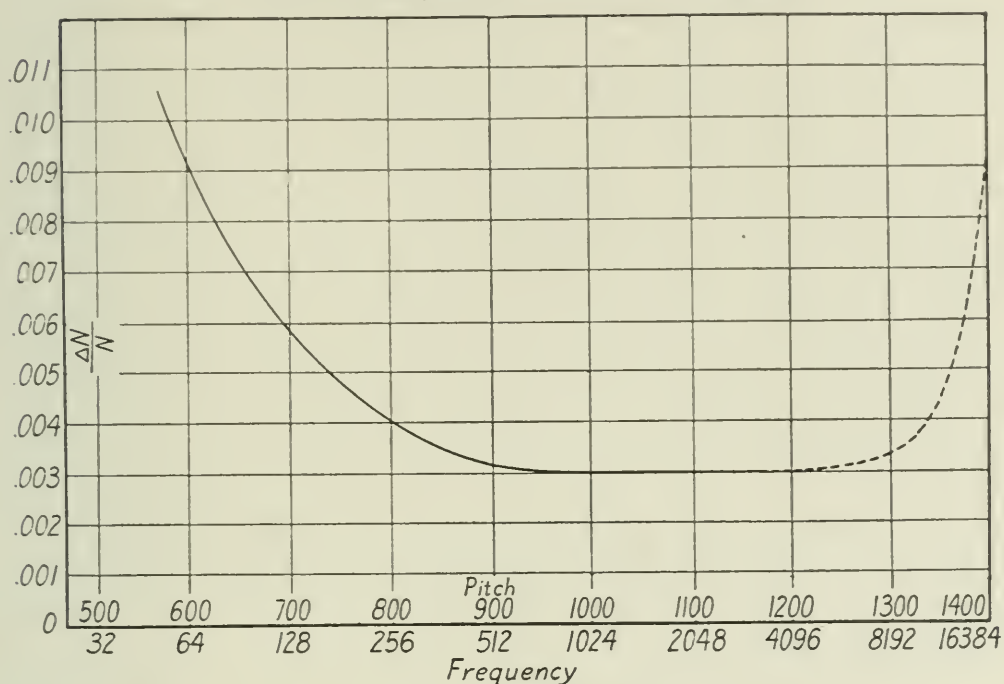
Minimum Perceptible Difference in Frequency

figure will be discussed later. For frequencies above 400 this fractional change is a constant equal to .003. This ratio probably becomes larger again for the very high frequencies. It was found that it varied with intensity in approximately the same way as that given for the energy ratio.

Using these values in connection with the auditory-sensation area, it is possible to calculate the number of pure tones which the ear can perceive as being different. For example, if, starting at the minimum audibility curve, ordinate increments are laid off along a constant pitch line, that are successively equal to the value of ΔE at the intensity position above the threshold, then the number of such increments between the upper and lower curves in Fig.

1 is equal to the number of pure tones of constant pitch that can be perceived as being different in volume. If the minimum and maximum audibility curves were plotted on an energy scale, the increment length ΔE near the maximum audibility curve would be a million million times longer than its length in the minimum audibility curve, whereas when they are plotted on a logarithmic scale, this increment length remains approximately constant, changing by less than a factor 2 for 90 per cent. of the distance across the auditory-sensation area. The calculation shows (see Appendix A) that the number of such increments on the 100-cycle frequency line is 270, that is, 270 tones having a frequency of vibration of 1000 cycles can be perceived as being different in loudness.

What has been said of the intensity scale applies equally well to the frequency scale. The calculation (see Appendix A) indicates that the number of tones that are perceivable as being different in pitch along the 10-dyne pressure line is approximately 1300.

If an ordinate increment corresponding to ΔE and an abscissa increment corresponding to ΔN be drawn, a small rectangle will be formed which may be considered as forming the boundary lines for a single pure tone. All tones which lie in this area sound alike to the ear. The number of such small rectangles in the auditory-sensation area corresponds to the number of pure tones which can be perceived as being different. The calculation (see Appendix A) of this number indicates that there are approximately 300,000 such tones.

One might well ask the question: How many complex sounds which are different can be sensed by the ear? At first thought, one might say that this number is represented by all the possible combinations of pure tones. Of course, such a number would be entirely too large, for some of these would sound alike to the ear, since the louder tones would necessarily mask the feebler ones. It is evident, however, that the number of such complex sounds will be very much larger than the number of pure tones.

It is seen that the use of the logarithmic scale in Fig. 1 is much more convenient not only on account of the large range of values necessary to represent the auditory-sensation area, but also because of its scientific basis. Psychologists have recognized this since Weber and Fechner formulated the relation between the sensation and the stimulus. Although logarithmic units have

been used by various authors in measuring the amount of sensation, the numerical values have been quite different. It seems inevitable that there will be a greater coöperation in the future between men in the various branches of science working on this subject, so, in order to avoid misunderstanding, it would be very advantageous for all to use, as far as possible, the same units. With this in mind, I am taking the liberty of suggesting for discussion units for both loudness and pitch.

In the telephone business, the commodity being delivered to the customers is reproduced speech. One of the most important qualities of this speech is its loudness, so it is very reasonable to use a sensation scale to define the volume of the speech delivered. At the present time, an endeavor is being made to obtain an agreement of all the telephone companies, both in the United States and abroad, to adopt a standard logarithmic unit for defining the efficiency of telephone circuits and the electrical speech levels at various points along the transmission lines. The *chief interest* in changes in efficiency of transmission apparatus is their effects upon the loudness of the speech delivered by the receiver at the end of the telephone circuit. So it would be very advantageous to use this same logarithmic scale for measuring differences in loudness.

This scale is chosen so that the loudness difference is ten times the common logarithm of the intensity ratio. This means that if the intensity is multiplied by a factor 10, the loudness is increased by ten; if the intensity is multiplied by 100, the loudness is increased by 20; if the intensity is multiplied by 1000, the loudness is increased by 30, etc. It was seen above that under the most favorable circumstances a change in loudness equal to 1/2 on this scale could just be detected. Knudsen's data indicates, however, that when a silent interval of only two seconds intervenes between the two tones being compared, a loudness change greater than unity on this scale is required before it is noticeable. So the smallest loudness change that is ordinarily appreciated is equivalent to one unit on this scale. It is also convenient because of the decimal relation between loudness change and intensity ratio. This relation is expressed by the formula:

$$\Delta L = L_1 - L_2 = 10 \log_{10} \frac{I_1}{I_2} \text{ or } \frac{I_1}{I_2} = 10^{\frac{\Delta L}{10}}$$

where L_1 and L_2 are the two loudness values corresponding to the intensities I_1 and I_2 . Since intensities of sound are proportional to the square of pressure amplitudes this may also be written:

$$\Delta L = 20 \log \frac{p_1}{p_2}$$

The most convenient choice of the intensity or pressure used as a standard for comparison depends upon the problem under consideration. In the sensation area chart of Fig. 1, the intensity line corresponding to one dyne was used as the zero level, that is, p_2 was chosen equal to 1 so that

$$\Delta L = 20 \log p$$

The choice of the base of logarithms for the pitch scale is dictated by the fact mentioned before, that the ear perceives octaves as being very similar sensations. Consequently the base 2 is the most logical choice for expressing pitch changes. If the logarithm of the frequency to the base 2 were used, perceptible changes in pitch would correspond to inconveniently small values of the logarithm. It is better to use the logarithm to the base $\sqrt[100]{2}$ which is 100 times as large. On this scale the smallest perceptible difference in pitch is approximately unity—somewhat more for frequencies greater than 100 cycles or somewhat less for lower frequencies, according to Knudsen's data. The scale on the charts is chosen so that the change in pitch is given by

$$\Delta P = 100 \log_2 N$$

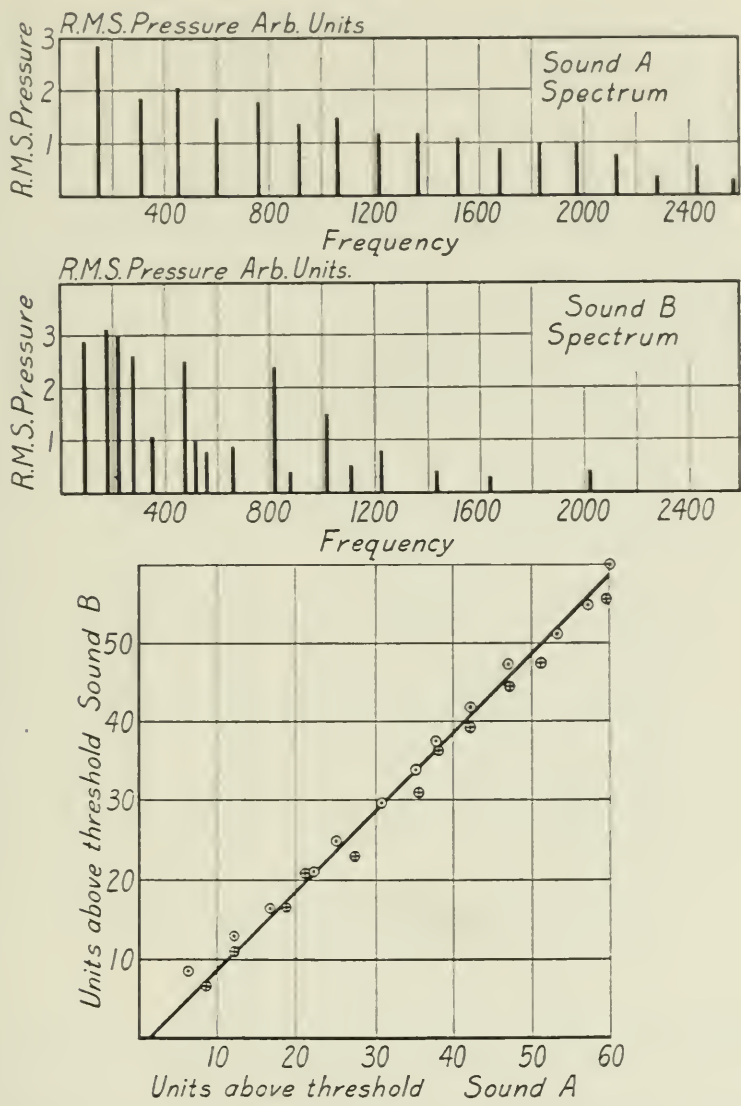
where N is the frequency of vibration.

It is now evident why such pitch and loudness scales were used in Fig. 1. With these scales, the number of units in any area gives approximately the number of tones that can be ordinarily appreciated in that area. For example, there are approximately 2000 distinguishable tones in each square, there being more near the centre and fewer near the boundary lines than this number.

Experiments have shown that pure tones of different frequencies which are an equal number of units above the threshold value sound equally loud. This statement may require modification when very loud tones are compared, but the data indicated that throughout the most practical range this was true. Consequently, the absolute loudness of any tone can be taken as the number of units above the threshold value.

In the measurement of the loudness of complex tones, the situation is not so simple. It has been found that if two complex tones are judged equally loud at one intensity level and then each is magnified equal amounts in intensity, they then may or may not sound equally loud. The curves shown in Figs. 4, 5 and 6

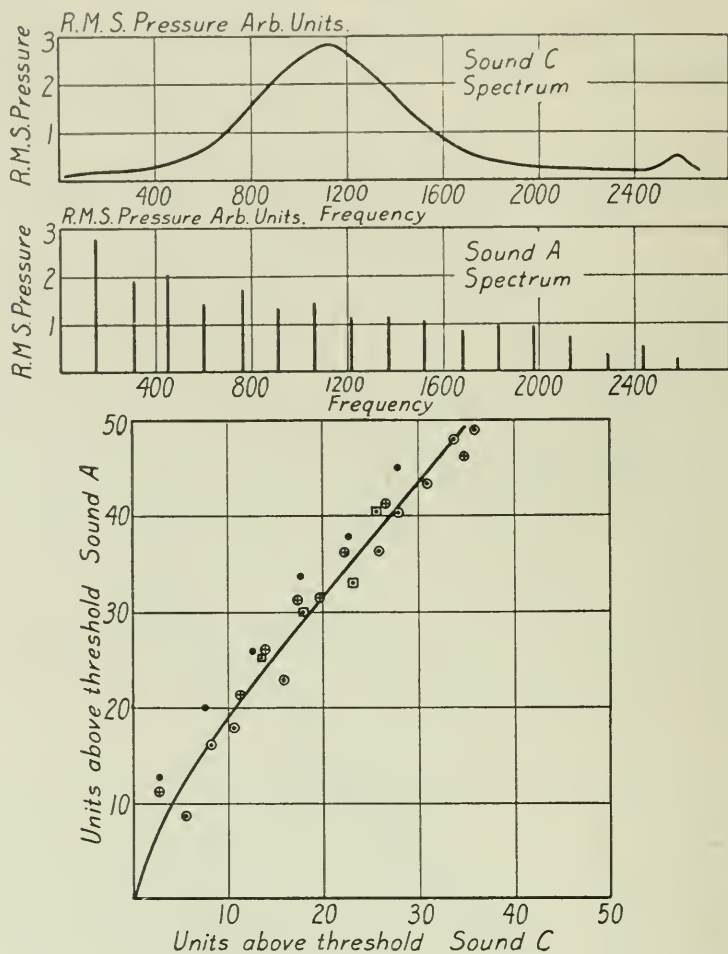
FIG. 4.



will illustrate this. The first (Fig. 4) shows the comparisons at different intensity levels of two sounds whose pressure spectra are shown in the two figures at the top. The x-axis gives units above threshold for sound *A* and the y-axis gives the units above threshold of the sound *B* when the two sound equally loud. In this case, the spectra are somewhat similar and we have a straight

line of slope 45° passing nearly through the origin. The two sounds are thus of practically equal loudness when they are the same number of units above threshold. In Fig. 5 we have similar data for two sounds which have quite different spectra as is indicated by the two charts at the top. The curve for *C* means

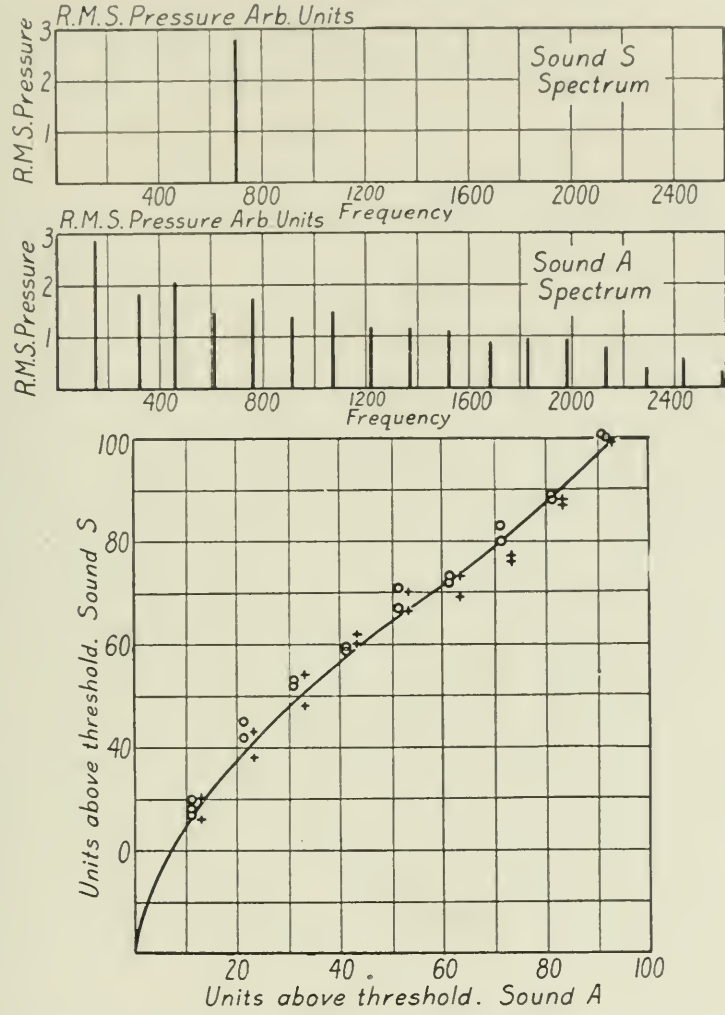
FIG. 5.



that it was a practically continuous spectrum. It was produced by a device for making the "swishing" type of noises which are usually so prominent in office rooms. The curve representing the relation is not straight, since for values of intensity near the threshold, the loudness increases faster for the *C* sound for increments in the intensity than for the *A* sound. For example it is seen that when the sound *C* is 30 units above the threshold, the sound *A* is 45 units above the threshold when the two sound equally loud. In Fig. 6 a comparison is given between the loud-

ness of a pure tone of 700 cycles and a complex sound designated by *A* in the last figure. In this case again the relation is expressed by a curve. The technic of making such loudness measurements is rather difficult and requires a large number of observations before the values are reliable. A paper on this subject which will

FIG. 6.



soon be published will give a detailed account of this work on loudness.

Enough data have been given to show that in order to give loudness a definite meaning for complex sounds, a more precise definition is necessary. It has been found convenient to define the loudness of any complex or pure tone in terms of the loudness of a sound standard. This standard is a pure tone having a vibration frequency of 700 cycles per second. Its abso-

lute loudness is defined as the change in loudness measured on the scale defined above, from the loudness value corresponding to the threshold pressure for normal ears which for 700 cycles is exactly 0.001 dyne. This frequency was arbitrarily chosen as a standard for measuring loudness because of this particular value of its threshold pressure, and because it is close to the frequency at which the loudest tones used in conversational speech occur. By this definition, the loudness of a tone of frequency 700, for which p is the pressure variation, expressed as a root mean square value,

$$L = 60 + 20 \log p$$

and the loudness of any other sound, pure or complex, is defined as being equal to that of a tone of frequency 700, seeming equally loud. Such a definition implies that experimental measurements can be made to determine when any complex sound is equally loud to a 700-cycle tone. Such measurements can be made although the observational error is rather large and the judgment of various individuals is sometimes quite different, which means only that loudness as measured by various individuals is different. For use in engineering work, however, the average of a large number of individuals can be taken and this loudness will have a definite determinable value. For example in Fig. 6, the loudness of the A sound when it is 60 units above the threshold is 72, since it sounds as loud as a 700-cycle tone which is 72 units above its threshold. The loudness of complex sounds usually increases faster with increases in intensity than that of pure tones. This would be expected since the threshold is determined principally by the loudest frequency in the complex sound and as the intensity is increased the other frequencies begin to add to the total loudness.

Since pure tones of different pitches which are the same number of units above the threshold sound equally loud their loudness L can be represented by the formula

$$L = L_0 + 20 \log p$$

where p is the root mean square value of the pressure amplitude produced in the ear by the tone and L_0 is the number of units from the 1-dyne line to the minimum audibility curve. The values of L_0 can be read directly from the chart in Fig. 1.

The choice of the loudness and pitch units used above leads to a *rational definition of the degree of deafness*.

The number of possible pure tones that can be sensed by a deaf person is considerably smaller than that mentioned above obtained from the normal auditory-sensation area. A logical way of defining the amount of hearing is: *To give the per cent. of the total number of distinguishable pure tones audible to a person with normal hearing, that can be sensed by the deaf person.*

Some definition of this sort will be very helpful in clearing up the confusion that now exists in court cases involving the degree of deafness. It is well known that there are a number of laws which prevent people who have more than a defined amount of deafness from doing certain classes of work. For example, one cannot operate an automobile if he has a certain per cent. of deafness. At the present time, there is a large variation between the standards set up by the various doctors in different parts of the country.

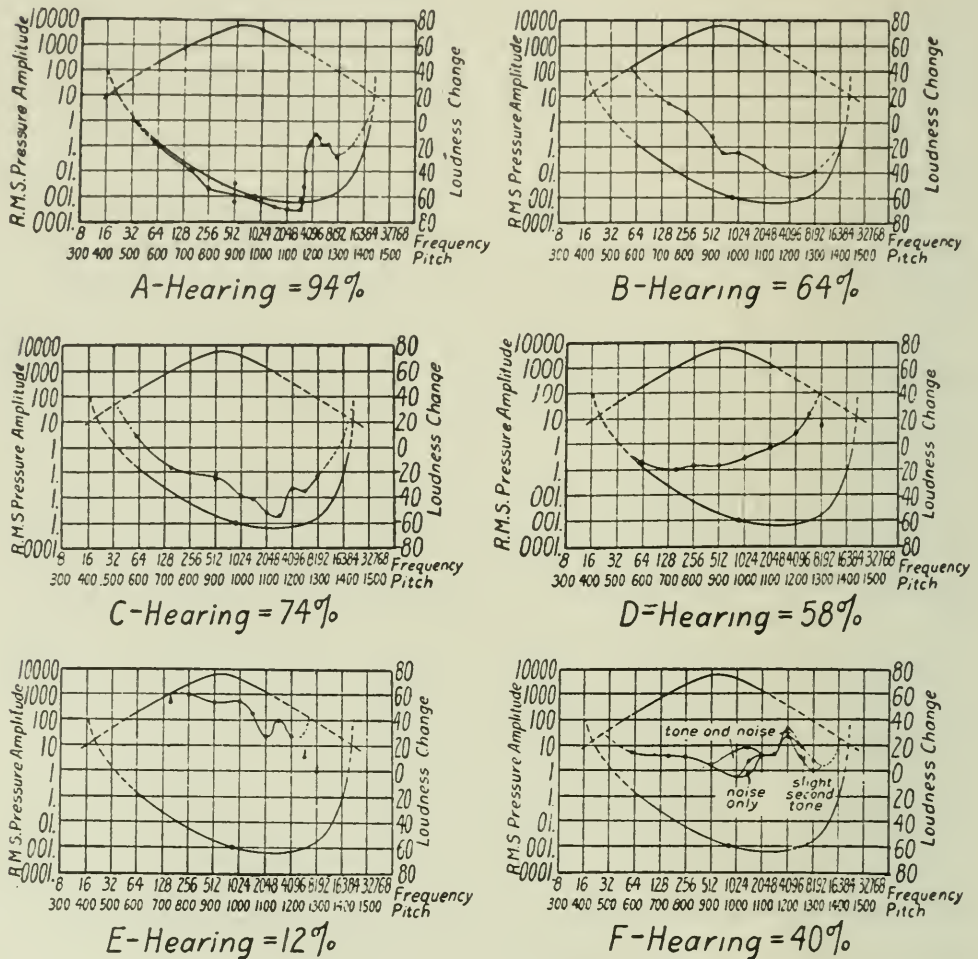
From the discussion above it was seen that the number of tones corresponding to any region was approximately proportional to the area of that region when the logarithmic units were used. Consequently the per cent.* of hearing can be taken as the fractional part of the normal auditory-sensation area in which tones can be properly sensed. The per cent. of deafness is of course 100 minus the per cent. of hearing.

To emphasize the meaning of this definition, some audiograms, that is minimum audible intensity curves, for some typical cases of deafness will be given. These are shown in Fig. 7. The first chart shows a common type of deafness in which the sensitivity to the high frequencies suddenly decreases, as is indicated by the rise in the minimum audible intensity curve when the frequency exceeds 3000 cycles per second. The sensation area for this person is 94 per cent. of that for the average. Consequently, his per cent. of hearing is 94 per cent. It is also convenient to speak of the per cent. of hearing for each pitch. It is evident that the logical definition for this is the ratio of the widths of the sensation area for the person tested and normal person, measured along the ordinate drawn at the frequency in question.⁵⁶ For

* This assumes that the Fechner ratio for pitch and loudness is approximately the same for one having abnormal as for one having normal hearing.

example, in this audiogram the person had more than 100 per cent. hearing for most of the pitch range. At 4000 cycles, however, the per cent. hearing was only 60 per cent. This means that for this pitch, the person when compared with one having nor-

FIG. 7.



Audiograms for typical cases of deafness.

mal hearing could sense only 60 per cent. as many gradations in tonal volume before reaching the threshold of feeling.

The second chart corresponds to a type of deafness that is not so common. It shows relatively large losses at the lower frequencies. The per cent. hearing in this case is seen to be 64 per cent.

The third type is very common and corresponds to a general lowering of the frequencies throughout the entire pitch range. In these first three cases, the deaf persons could carry on a con-

versation without any difficulty whatever. In the last two of these, difficulty was experienced in understanding a speaker at any considerable distance. In the first case, the person could not hear the steam issuing from a jet or any other high hissing sound. However, he could hear and understand speech practically as well as anyone with normal hearing.

The fourth case shows a falling off at the high frequencies, but this loss in hearing proceeds gradually as the pitch increases rather than abruptly as in the first case. As indicated in the figure the per cent. of hearing is 58 per cent.

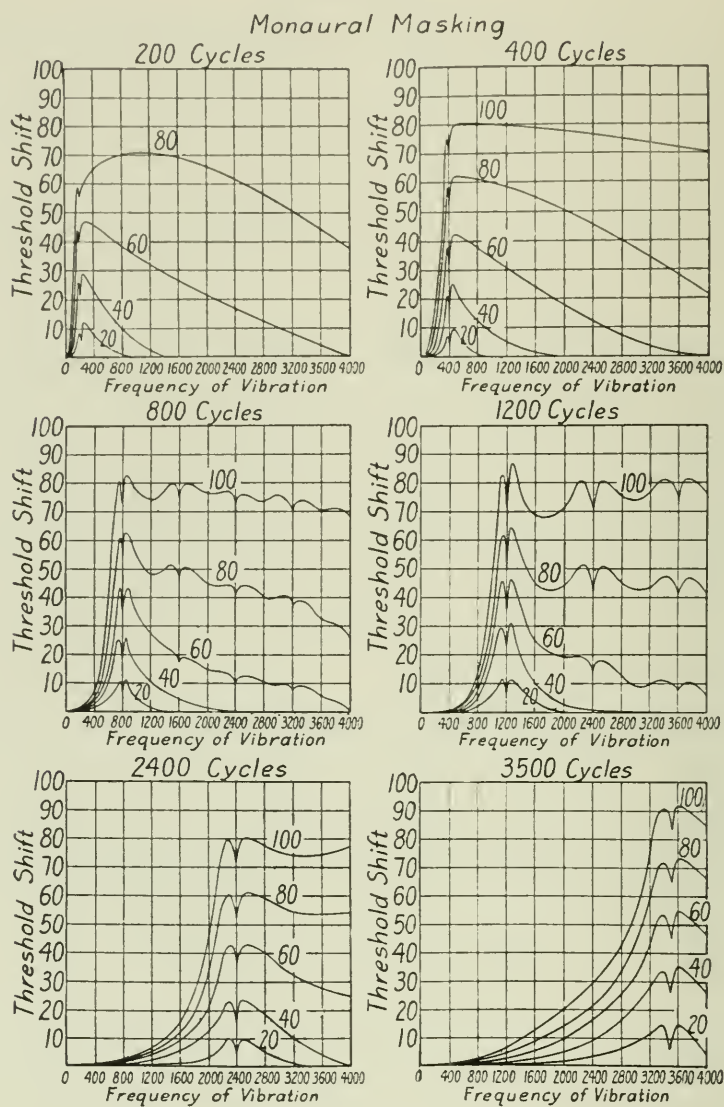
The fifth case is one of extreme deafness and is typical of such cases. The per cent. of hearing is only 12 per cent. The last case shows not only the minimum audibility curve, but the quality of the sensation perceived. As indicated on the chart, in certain regions noises are heard when the stimulus is a pure tone. When computing the per cent. of hearing in such cases, it seems reasonable to take only the area where sensation of good quality is perceived. In some cases, this poor quality extends through practically the whole area and although the person hears sounds, he is unable to properly interpret them. Consequently, from a practical point of view, his per cent. of hearing is very low. For such cases, deaf sets or other aids to the hearing do not give any satisfactory help.

We are now in a position to discuss another set of facts concerning the perception of tones, namely, the ability of the ear to perceive certain sounds in the presence of other sounds. Such data for pure tones have been obtained in our laboratories and will soon be published in some detail. The apparatus used consisted simply of two vacuum tube oscillators generating the two tones used and two attenuators which made it possible to introduce the tones into a single receiver with any desired intensities. In other words, it consists of two audiometers with a common receiver for generating the two tones. The curves shown in Fig. 8 give the general character of the results of this work.

The ordinates show the amounts in loudness units that the threshold value of a tone of any given frequency called the "masked tone" is shifted due to the presence of another tone called the "masking tone." The frequency of the masking tone is given at the top of each set of curves.

The experimental procedure was as follows: The threshold values for the two tones were first determined. The intensity of the masking tone (the frequency of which is given above each graph) was then increased beyond its threshold value by the num-

FIG. 8.



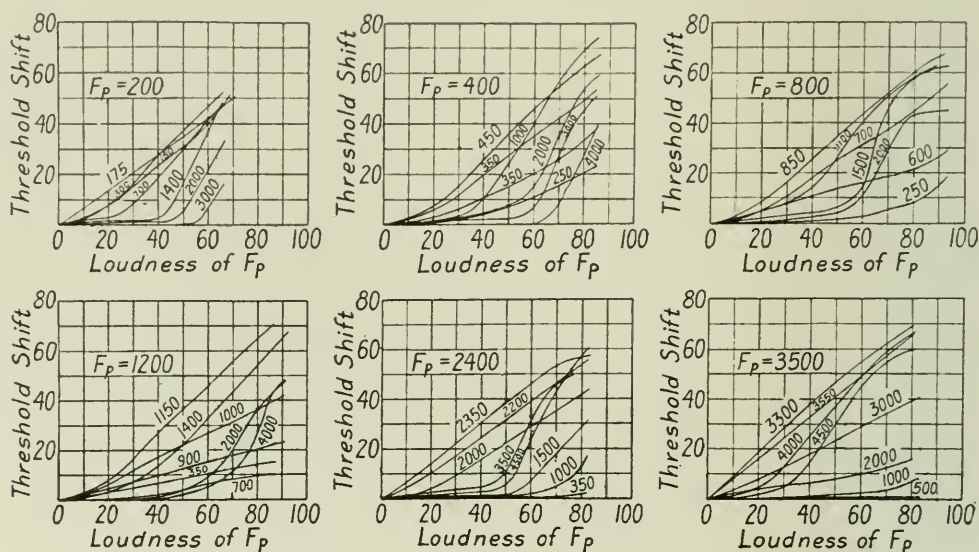
ber of units indicated just above the curve. The masked tone was then increased in intensity until its presence was just perceived. The amount of this latter increase, measured on the loudness scale is called the *threshold shift* and is plotted as ordinate in Figs. 8, 9 and 10. The frequencies of the masked tones are given by the abscissæ.

For example, in the fourth chart, the masking effects of the tone having a frequency of 1200 cycles are shown. It is seen that the greatest masking effect is near 1200 cycles, which is the frequency of the masking tone. A tone of 1250 cycles must be raised to 46 units above the threshold to be perceived in the presence of a 1200-cycle tone which is 60 units above its threshold, or it must be raised to within 14 units of the masking tone before it is perceived. This corresponds to an intensity ratio between the tones of only 25. A tone of 3000 cycles, however, can be perceived in the presence of a 1200-cycle tone which is 60 units loud when it is only 8 units above its threshold. This means that the intensity ratio between these two tones, under such circumstances, corresponds to 52 units or to a ratio of approximately 160,000 in intensity. However, as the loudness of the masking tone is increased, all of the high tones must be increased to fairly large values before they can be heard. For example, the high frequencies must be raised 75 units above the threshold to be heard in the presence of a 1200-cycle tone having a loudness of 100 units. But even for such large intensities for the masking tone, those frequencies below 300 are perceived by raising their loudness only slightly above the threshold value. It should be noticed that in all cases, those tones having frequencies near the masking frequency, whether they are higher or lower, are easily masked.

It is thus seen that Mayer's conclusion that a low pitch sound completely obliterates higher pitched tones of considerable intensity and that higher pitched frequencies will never obliterate lower pitched tones is true only under certain circumstances. A low tone will not obliterate to any degree a high tone far removed in frequency, except when the former is raised to very high intensities. Also a tone of higher frequency can easily obliterate a tone of lower frequency if the frequencies of the two tones are near together. When the two tones are very close together in pitch the presence of the masked tone is perceived by the beats it produces. This accounts for the sharp drop in the curves at these frequencies. A similar thing happens for those regions corresponding to harmonics of the masking frequency. In the charts for the 200- and 400-cycle masking tones these drops are not shown inasmuch as they were small, but in an accurate picture they should be shown.

In Fig. 9, these results are shown plotted in a different way. The abscissæ represent the loudness of the primary tones whose frequency is indicated at the top of each of the charts. The amounts that the threshold is shifted are plotted as ordinates as in the previous figure. For example, in Chart 1, the results are shown for a masking tone of 200 cycles. The curve marked 3000 indicates the masking effect of a 200-cycle upon a 3000-cycle

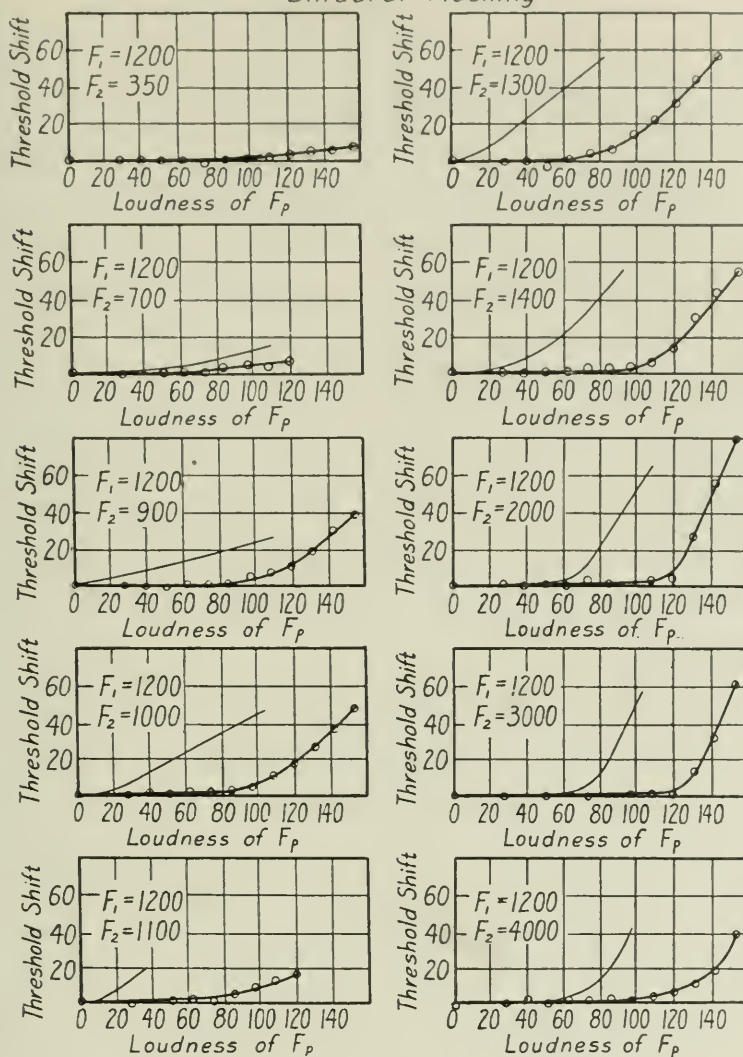
FIG. 9.
Monaural Masking



tone. It is seen that the loudness of the low pitched tone can be raised to 55 units before it has any interfering effect upon the high pitched tone. For louder values than this it has a very marked effect. It will be noticed that in nearly all of the charts the curves for different frequencies intersect. This leads to some rather interesting conclusions regarding the perception of a complex tone. For example, consider the curves for a masking tone having a frequency of 400 cycles. Assume we have a complex tone having three frequencies of 400, 300 and 200 cycles with relative loudness values of 50, 10 and 10, respectively. The ear will hear only the 400-cycle tone and the 2000-cycle tone as is evident from the curves. It would be necessary to raise the 300-cycle tone above 16 units for it to be heard in the presence of 400 cycles of loudness 50. However, if the sound is magnified without distortion 30 loudness units, so that these three frequencies have loudness values of 80, 40 and 40, respectively, then the

400-cycle tone and 300-cycle tone only will be heard. Under such conditions, the 300-cycle tone could be attenuated approximately 15 units before it would disappear. This means that the sensation produced by a complex sound is different in character as

FIG. 10.
Binaural Masking



well as in intensity when the sound is increased or decreased in intensity without distortion. In general, as the tone becomes more intense the low tones become more prominent because the high tones are masked. It is a common experience of one working with complex sounds to have the low frequencies always gain in prominence as the sound is amplified.

The question naturally arises, "Does the same interfering effect exist when the two tones are introduced into opposite ears

instead of both being introduced into the same ear?" The answer is "No." Curves showing the results in such tests are shown in Fig. 10. For comparison the results for the case when the tones are both in the same ear are given by the light lines. Take the case of 1200 and 1300 cycles. It is rather remarkable that a tone in one ear can be raised to 60 units, that is, increased in intensity one million times, before the threshold value for the tone in the other ear is noticeably affected. If the 1300-cycle tone were introduced into the same ear as the 1200-cycle tone, its loudness would need to be shifted 40 units, corresponding to a 10,000-fold magnification in intensity above its threshold intensity in the free ear before it can be heard. It is seen that if one set of curves is shifted about 50 units it will coincide with the second set. This strongly suggests that the interference in this case is due to the loud tone being transmitted by bone conduction through the head with sufficient energy to cause masking. The vibration is probably picked up by the base of the incus and transmitted from there to the cochlea in the usual way. There is other evidence* which I shall not have space here to discuss, which indicates that the effective attenuation from one ear to the other is approximately 50 units.

With these facts in mind, we are now ready to discuss the theory of hearing which will best account for them. I will refer briefly to just a few of the principal theories of hearing which have been proposed. The sketch shown in Fig. 11 gives a diagrammatic picture of the internal ear. In the Helmholtz theory, as first formulated, it is stated that the organ of Corti located between the basilar membrane and the tectorial membrane act like a set of resonators which are sharply tuned. Each tone stimulates a single organ depending upon its pitch. Later this theory was somewhat modified as it was thought that the resonant property might reside in one of the membranes in the cochlea.

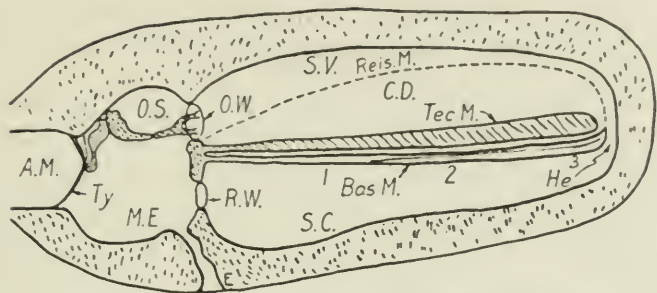
In the "telephone" theory, as expounded by Voltalini, Rutherford, Waller and others, it is assumed that the basilar membrane vibrates as a whole like the diaphragm of a telephone receiver,

* See paper by Wegel and Lane soon to be published in the *Physical Review* entitled "The Auditory Masking of One Pure Tone by Another and Its Relation to the Dynamics of the Inner Ear."

and consequently responds to all frequencies with varying degrees of amplitude. The discrimination of pitch takes place in the brain.

Meyers in his theory states that various lengths of the basilar membrane are set in motion depending upon the intensity of the stimulating tone. As in the previous theory, the pitch discrimination is accomplished in some way in the brain.

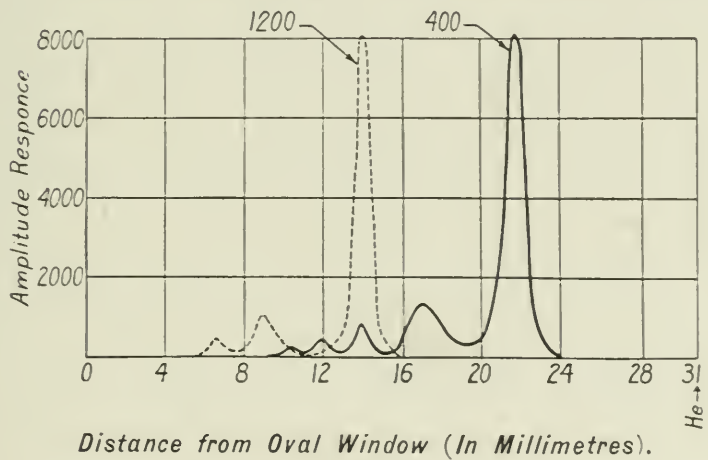
FIG. 11.



Diagrammatic representation of auditory function.

A. M.	Auditory meatus	O. W.	Oval window
Bas. M.	Bas. mem. including organ of Corti	Reis. M.	Reissner's mem.
C. D.	Cochlear duct	R. W.	Rd. window
E.	Eustachian tube	S. C.	Scala cochlea
He.	Helicotrema	S. V.	Scala vestibuli
M. E.	Middle ear	Tec. M.	Tectorial membrane
O. S.	Ossicles (malleus, incus, stapes)	Ty.	Tympanic membrane

Response of Basilar Membrane for Loudness of 80.



In the "non-resonant" theory of Emile ter Kuile it is assumed that the sound disturbance penetrates different distances into the cochlea depending upon the frequency of the stimulating tone. The further along the membrane the disturbance reaches, the lower will be the pitch sensation. A low pitch tone then stimulates all of the nerve fibres that would be stimulated by tones of higher pitch plus some additional nerve fibres.

The theory of maximum amplitudes was first put into definite form by Gray in 1899.⁶⁹ It assumes that the position of maximum amplitude of the basilar membrane varies with the pitch of the stimulating tone. Although a considerable portion of the membrane vibrates when stimulated by a pure tone, the ear judges the pitch by the position of maximum response of the basilar membrane. Roaf has shown that some action of this sort must take place due to the dynamical constants involved.⁶¹ It is an amplification of this theory that I desire to propose as the one which most satisfactorily accounts for the facts.

When a sound wave impinges upon an ear-drum, its vibrational motion is communicated through the middle ear (Fig. 11) by means of the chain of small ossicles (malleus, incus and stapes) to the oval window. Here the vibration is communicated to the fluid contained in the cochlea. If the pitch of the tone is low, say below 20 vibrations, the fluid is moved bodily back and forth around the basilar membrane through the helicotrema, the motion of the membrane at the round window and the oval window being just opposite in phase, the former moving inward while the latter moves outward. For very high frequencies, the mass reactions of the ossicles and the fluid are so great that very little energy can be transmitted to the cochlea. For example, when the elastic forces are negligible it requires a force 10,000 times as large to produce the same amplitude of vibration at 10,000 cycles as that required at 100 cycles. For intermediate frequencies the mass reactions, the elastic restoring forces and the frictional resistances which are brought into play are such that the wave is transmitted through the basilar membrane causing the nerves to be excited.

It is thus seen that the upper and lower limits of audibility are easily explained. When the forces upon the drum of the ear or walls of the ear canal are large enough to excite the sensation of feeling and the pitch of the tone is either too low or too high to cause any perceptible vibration of the basilar membrane, we are beyond the lower or upper limit of audibility respectively. At frequencies between these limits, the vibrational energy is first communicated to the fluid in the scala vestibuli and then transmitted through the two membranes into the fluid of the scala cochlea. As the basilar membrane transmits the sound wave it takes up a vibration amplitude which stimulates the nerve

fibres located in it. The entire membrane vibrates for every incident tone, but for each frequency there is a corresponding spot on the membrane where the amplitude of the vibration is greater than anywhere else. Our postulate is that only those nerves are stimulated which are at the particular parts of the membrane vibrating with more than a certain critical amplitude; and that we judge the pitch from the part of the membrane where the nerves are stimulated. According to this conception, the variation with frequency of the minimum audible intensity is due principally to the variation with frequency of the transmission efficiency of the mechanical system between the auditory meatus and the basilar membrane. Pure tones of equal loudness correspond either to equal amplitudes or to equal velocities of vibration of the basilar membrane or to some function of the two. Whatever is assumed, the dependence of the minimum audible intensity upon frequency for the ear can be explained entirely by the vibrational characteristics of the ear mechanism. For the sake of clearness it will be assumed that equal amplitudes of vibration of the basilar membrane correspond to equal sensations. For loud pure tones, there are several regions of maximum amplitude on the membrane, corresponding to the tone and to the harmonic introduced by the non-linear response of the middle ear, the latter maxima increasing very rapidly as the stimulation increases.

It is a strange thing that the phenomenon of the masking of tones which, as stated in the beginning, has been considered by some to be so fatal to any resonator theory, is the very thing that has furnished experimental data which makes it possible to calculate the vibration characteristics of the inner ear. Such a calculation must be based upon assumptions which will be uncertain, but will seem reasonable. It is not my purpose to discuss those here, but I shall give only the final result of such a calculation made by Mr. Wegel and Mr. Lane of our laboratories. At the bottom of Fig. 11, the two curves show the amplitude of vibration of different portions of the basilar membrane for the two frequencies 400 and 1200 cycles. For purposes here these curves may be considered to be simply illustrative. This membrane has a length of 31 mm. and a width of .2 mm. at the base and .36 mm. at the helicotrema end. The x-axis in this figure gives the dis-

tance in millimetres from the oval window and the y-axis gives the amplitudes of vibration in terms of the amplitude corresponding to the threshold of audibility. The loudness of the stimulating tones in both cases is 80 units. It will be seen that the maximum response for the high frequencies is near the base of the cochlea, while that for the low frequencies is near the helicotrema. It will be noticed that the amplitude of the membrane has several maxima corresponding to the subjective harmonics.

With this picture in mind, it is clear why the perception of one tone is interfered with by the presence of a second tone when their frequencies are close together, since the nerves necessary to perceive the first tone are already stimulated by the second tone. Also when their frequencies are widely separated, entirely different sets of nerves carry the impulses to the brain, and consequently there is no interference between the tones except that which occurs in the brain. Although this brain interference may not be entirely negligible, especially for very loud sounds, it is certainly very much smaller than that existing in the ear for tones close together in pitch.

It is also seen that the reason why the low tones mask the high tones very much more easily than the reverse is due to the harmonics introduced by the transmission mechanism of the ear. Inasmuch as these harmonics are due to the second order modulations, they are proportional to the square of the amplitude and, therefore, become much more prominent for the large amplitudes. When two tones are introduced, summation and difference tones as well as the harmonics will necessarily be present (see Appendix B). With the proper apparatus for generating continuously sounding tones, these subjective tones are easily heard. Their frequency can be quite accurately located by introducing from an external source a frequency which can be varied until it produces beats with the subjective tone.

Messrs. Wegel and Lane who are working in this field have observed modulation frequencies created in the ear as high as the fourth order. They will soon publish* an account of this work on the vibrational characteristics of the basilar membrane. It is seen that the quality as well as the intensity of the sensation produced by a pure tone should change as the intensity of stimulus

* Wegel and Lane, see paper already cited.

is increased due to the increasing prominence of the harmonics. This is in accordance with one's experience while listening to pure tones of varying intensity. The non-linear character of the hearing mechanism is also sufficient to account for the falling off in the ability of one to interpret speech when it becomes louder than about 75 units. The introduction of the summation and difference tones and the harmonics makes the interpretation by the brain more difficult. Its action in this respect is very similar to the carbon transmitter used in commercial telephone work or to an overloaded vacuum tube. This characteristic of the ear also explains why we should expect departures from non-linearity when making loudness balances for complex tones. It also suggests that a similar thing might be expected when comparing the loudness of pure tones if the balances are made at very high intensities. No such balances have yet been made.

What happens to the ear when one becomes deaf? This question, of course, is one for the medical profession to answer, but let us take one or two simple cases and see if they fit into this theory. First assume that the nerve endings are diseased for a short distance away from the base of the cochlea so that they send no impulses to the brain. Under certain assumptions the kind of an audiogram one should obtain can be calculated from the vibrational characteristics determined as mentioned above. Such a calculation shows that an audiogram similar to that shown in Fig. 4, which has a rapid falling off in sensitiveness, can be accounted for, both quantitatively as well as qualitatively. On a pure resonant theory corresponding to that first proposed by Helmholtz, a tone island would exist corresponding to the affected region for such a case. Although we have tested a large number of cases, no such islands have ever been found. When the intensity of the tone is raised sufficiently to bring the amplitude of the area containing the healthy nerve cells which are adjacent to the diseased portion to a value above that corresponding to the threshold, the tone will then be perceived.

Again assume that due to some pathological condition, the tissue around the oval window where the stapes join the cochlea has become hardened. Its elasticity will then be greatly increased so that vibrational energy at low frequencies will be greatly dis-

criminated against. For such a case, an audiogram similar to that shown in Fig. 7-B would be obtained.

A number of things can cause a general lowering of the ear sensitivity, such as wax in the ear canal, affections of the ear-drum, fixation of any of the ossicles, thickening of the basilar membrane, affections of the nerve endings or loss in nervous energy being supplied to the membrane, etc. However, one would expect that each type of trouble would discriminate, at least to some extent, against certain frequency regions so as to produce some characteristic in the audiogram. Ear specialists are beginning to realize the possibility of obtaining considerable aid in the diagnosis of abnormal hearing from such accurate audiograms.

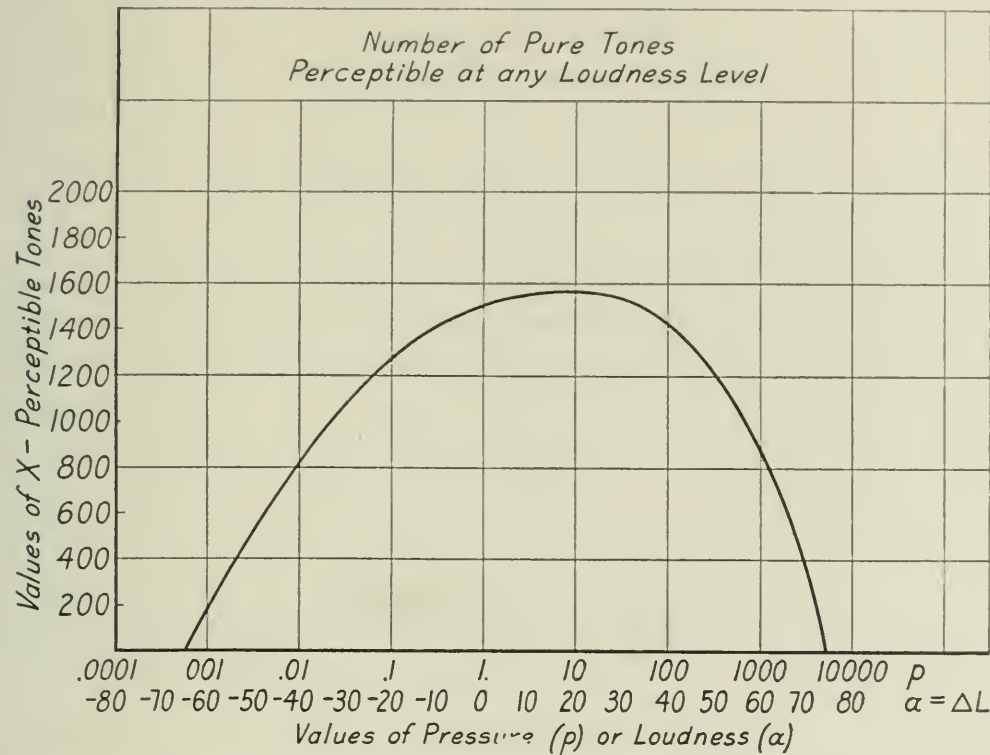
There are a large number of facts obtained from medical research which necessarily have a bearing upon the theory of hearing, but as far as I know none of them is contrary to the theory of hearing given above. It was seen that there are approximately 300,000 tone units in the auditory-sensation area. According to the anatomists, there are only 4000 nerve cells in the basilar membrane with four or five fibre hairs for each cell. Assuming that each hair fibre acts as a unit there are still insufficient units for each perceivable tone and according to the theory given above, a large number of these units must act at one time. Consequently the ear must be able to interpret differences in the intensity of excitation of each nerve cell as well as determine the position of each nerve cell excited.

Most modern neurologists believe in the "none or all" excitation theory of nerve impulses.⁵⁹⁻⁶⁰ They also claim that nerve impulses can never be much more rapid than about 50 per second and cannot therefore follow frequencies as high as those found in sound waves. The second statement only emphasizes the necessity of assuming that the intensity position as well as place position is necessary to account for the differentiation of pure tones. The first statement is not necessarily in conflict with such an idea since anatomists are not agreed upon the number of nerve fibres radiating from each nerve cell. Since each nerve fibre can serve to give a unit nerve impulse, the intensity of stimulation sent from a single nerve cell can increase with stimulation depending upon the number of nerve fibres brought into action. The intensity of the sensation produced is then directly related to the total number

of nerve fibres giving off impulses. It seems to me that the spacial and intensity configurations which are possible, according to this theory, are sufficient for an educated brain to interpret all the complex sounds which are common to our experience.

In conclusion then, it is seen that the pitch of pure tones is determined by the position of maximum response of the basilar

FIG. 12.



membrane, the high tones stimulating regions near the base and the low tones regions near the apex of the cochlea.

A person can sense two mixed tones as being distinctly two tones while he cannot sense two mixed colors, since in the ear mechanism there is a spacial frequency selectivity while in the eye mechanism there is no such selectivity.

The limiting frequencies which can be perceived are due entirely to the dynamical constants of the inner ear as is also the dependence of minimum audible intensity on frequency.

The so-called subjective harmonics, summation and difference tones are probably due to the non-linear transmission characteristics of the middle and inner ear.

These subjective harmonics account for the greater masking effect of low tones on high tones than high tones on low tones.

Due to this non-linear characteristic, the quality as well as the intensity of the sensation produced, especially by complex tones, change as the intensity of the stimulus increases.

The facts obtained from audiograms of abnormal hearing are consistent with the theory of hearing which has been outlined.

Although this theory of hearing involves the principle of resonance, it is very different from the Helmholtz theory as usually understood. In the latter it is assumed that there are four or five thousand small resonators in the ear, each responding only to a single tone; while in the former it is assumed that a single vibrating membrane which vibrates for every impressed sound is sufficient to differentiate the various recognizable sounds by its various configurations of vibration form.

A loudness scale has been chosen such that the loudness change is equal to ten times the common logarithm of the intensity ratio. A pitch scale has been chosen such that the pitch change is equal to 100 times the logarithm to the base two of the frequency ratio. The loudness of complex or simple tones is measured in terms of the number of loudness units a tone of 700 cycles must be raised above its average threshold value before it sounds equally loud to the sound measured.

The degree of deafness is measured by the fractional part of the normal area of audition in which the sensation is either lacking or false.

APPENDIX A.

The calculations of the number of pure tones perceivable as being different in pitch at a given intensity or being different in loudness at a given pitch involves a line integral. The calculation of the number of pure tones perceivable as being different either in loudness or pitch involves a surface integral.

Let the coördinates used in Fig. 1 corresponding to ΔL and ΔP be designated α and β , respectively. Then the relations shown in Figs. 2 and 3 can be expressed by the equations

$$(1) \quad \frac{\Delta E}{E} = f(\alpha - \alpha_0) \text{ and}$$

$$(2) \quad \frac{\Delta N}{N} = \varphi(\beta)$$

where α_0 is the value of α along the normal minimum audibility curve shown in Fig. 1. Knudsen data indicated that the curve

shown in Fig. 3 held only for values of $\alpha - \alpha_0$ corresponding to the flat part of the curve in Fig. 2. For lower intensities the pitch discrimination fell off in about the same way as that shown for the intensity discrimination. To represent this mathematically, $\varphi(\beta)$ can be multiplied by a factor which is unity for the loud tones and which increases similarly to $f(\alpha - \alpha_0)$ for the weaker tones. Such a factor is $10 f(\alpha - \alpha_0)$ since $f(\alpha - \alpha_0)$ is approximately $\frac{1}{10}$ for the louder tones. So the corrected formula for $\frac{\Delta N}{N}$ is

$$(3) \quad \frac{\Delta N}{N} = 10 \varphi(\beta) \cdot f(\alpha - \alpha_0)$$

Let dx be the number of perceivable tones of constant intensity corresponding to α in the pitch region between β and $\beta + d\beta$ and let dy be the number of perceivable tones of constant pitch corresponding to β in the region between α and $\alpha + d\alpha$. Then

$$(4) \quad dx = \frac{dN}{\Delta N}$$

$$(5) \quad dy = \frac{dE}{\Delta E}$$

But the values of α and β are given by

$$(6) \quad \beta = 100 \log_2 N$$

$$(7) \quad \alpha = 10 (\log_{10} E - \log_{10} E_1)$$

where E_1 is the value of intensity corresponding to a pressure amplitude of 1 dyne.

Substituting values of dN and dE in terms of α and β we have

$$(4') \quad dx = \frac{1}{100} \frac{N}{\Delta N} \log_e 2 d\beta = \frac{\log_e 2}{1000} \frac{d\beta}{\varphi(\beta) \cdot f(\alpha - \alpha_0)}$$

$$(5') \quad dy = \frac{1}{10} \frac{E}{\Delta E} \log_e 10 d\alpha = \frac{\log_e 10}{10} \frac{d\alpha}{f(\alpha - \alpha_0)}$$

The number of tones of constant intensity which are perceivable as different in pitch is then

$$x = \frac{\log_e 2}{1000} \int_{\beta_1}^{\beta_2} \frac{d\beta}{\varphi(\beta) \cdot f(\alpha - \alpha_0)}$$

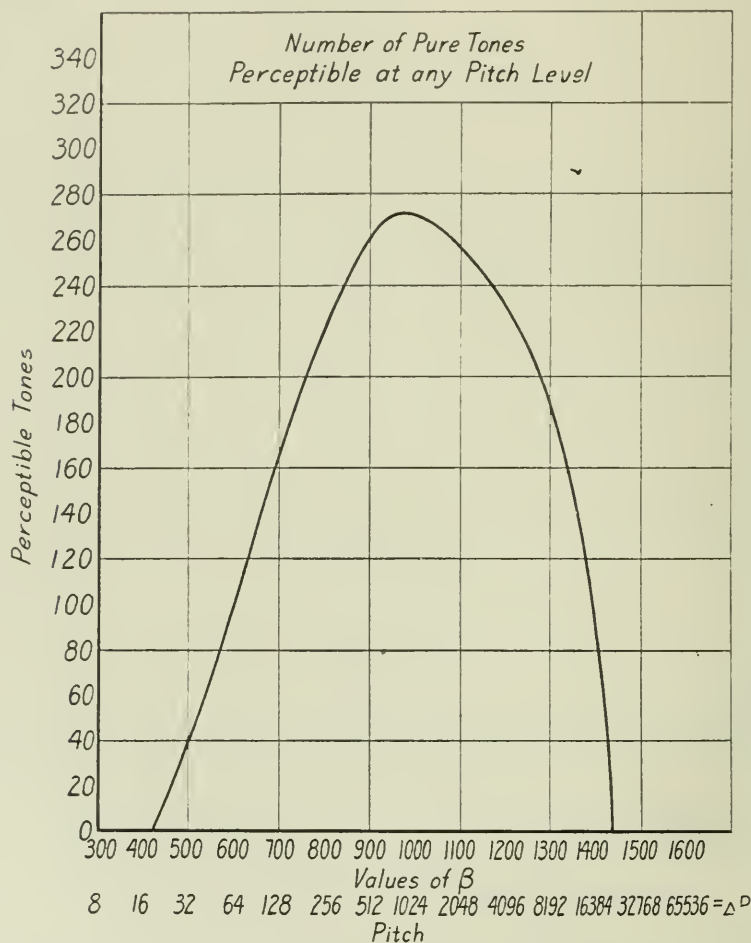
where β_1 and β_2 are the points where the particular intensity line cuts the boundary lines of the auditory-sensation area. For example, the limits for the line corresponding to 1-dyne pressure

amplitude are 500 and 1420. Similarly the number of tones of constant pitch which are perceivable as being different in loudness is given by

$$y = \frac{\log_2 10}{10} \int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{f(\alpha - \alpha_0)}$$

where α_1 and α_2 are determined by the intersection of the particular pitch line with the boundary lines of the auditory-sensation area.

FIG. 13.



The values of these integrals were computed graphically. Figs. 12 and 13 show the results of these calculations. It is seen that the maximum number of tones perceivable as different in loudness is in the frequency range 700 to 1500 which is also the important speech range. The number in this range is approximately 270.

In the pressure range from 1 to 100 there are approximately 1500 tones which can be perceived as being different in pitch.

FIG. 14.

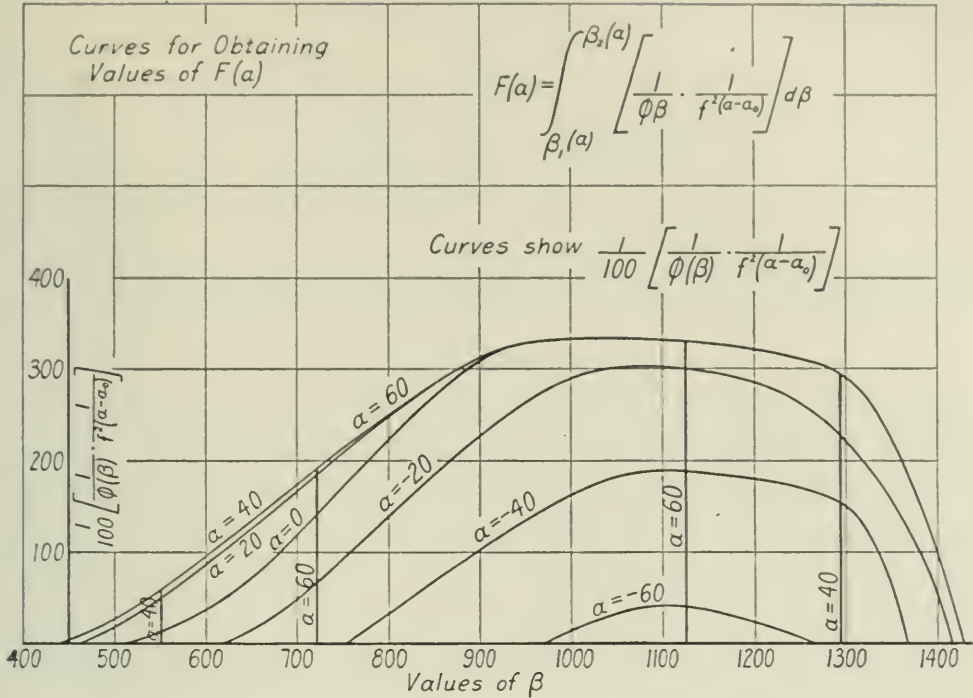
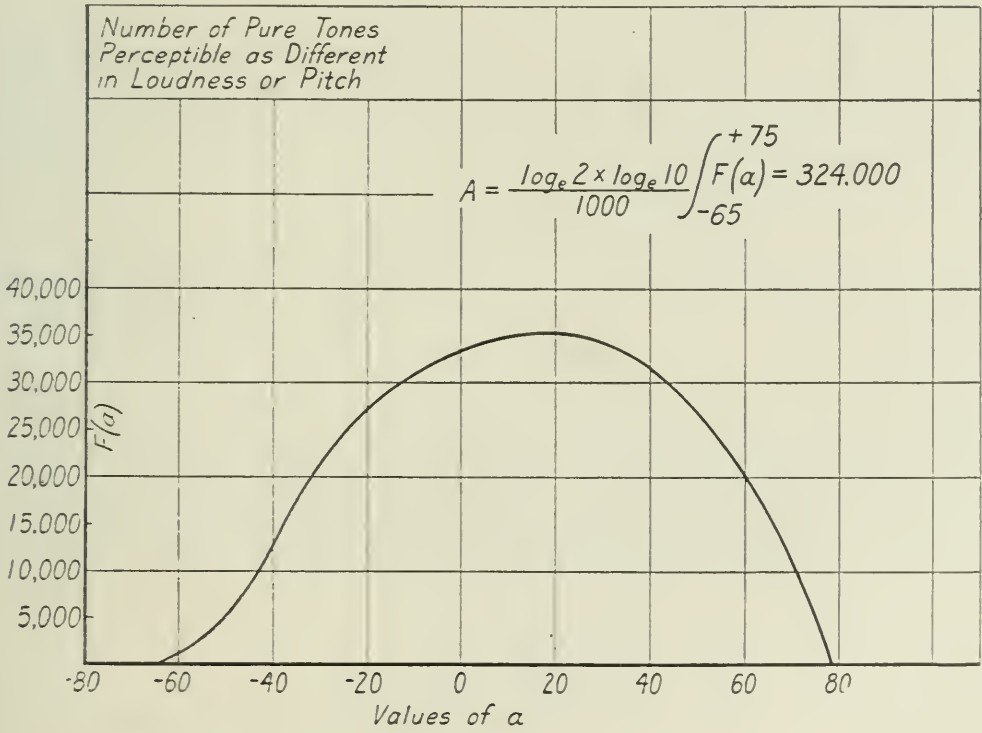


FIG. 15.



The number of tones ΔT in a small area $d\beta \, d\alpha$ situated with one corner at the point (α, β) is given by $d\alpha \, d\beta$ or

$$\Delta T = d\alpha \, d\beta = \frac{\log_e 2 \log_e 10}{10,000} \frac{d\alpha \, d\beta}{\varphi(\beta) f^2(\alpha - \alpha_0)}$$

$$T = \frac{\log_e 2 \log_e 10}{10,000} \iint \frac{d\alpha \, d\beta}{\varphi(\beta) f^2(\alpha - \alpha_0)}$$

The function $\frac{1}{\varphi(\beta) \cdot f^2(\alpha - \alpha_0)}$ must be integrated throughout the auditory-sensation area. This was done by graphical methods as shown in Figs. 14 and 15 with the result that $T = 324,000$.

APPENDIX B.

Let the pressure variation of the air in front of the drum of the ear be designated by δp . Since the pressure of the air in the middle ear balances the undisturbed outside air pressure this change in pressure multiplied by the effective area of the ear-drum is the only effective force that produces displacements. Let the displacement of the fluid of the cochlea near the oval window be designated by X . If Hookes law held for all the elastic members taking part in the transmission of sound to the inner ear then

$$(1) \quad X = k\delta p$$

where k is a constant.

It would be expected from the anatomy of the ear that Hookes law would start to break down even for small displacements. So in general the relation between the force δp and the displacement X can be represented by

$$(2) \quad X = f(\delta p) = a_0 + a_1\delta p + a_2(\delta p)^2 + a_3(\delta p)^3 + \dots$$

where the coefficients $\alpha_0, \alpha_1, \alpha_2 \dots$ belong to the expansion of the function into a power series. Now if δp is a sinusoidal variation then

$$(3) \quad \delta p = p_0 \cos \omega t$$

where $\frac{\omega}{2\pi}$ is the frequency of vibration. Substituting this value in (2), terms containing the cosine raised to integral powers are obtained. These can be expanded into multiple angle functions. For example, for the first four powers

$$(4) \quad \cos^2 \omega t = \frac{1}{2} \cos 2 \omega t + \frac{1}{2}$$

$$(5) \quad \cos^3 \omega t = \frac{1}{4} \cos 3 \omega t + \frac{3}{4} \cos \omega t$$

$$(6) \quad \cos^4 \omega t = \frac{1}{8} \cos 4 \omega t + \frac{1}{2} \cos 2 \omega t + \frac{3}{8}$$

It is evident then that the displacement X will be represented by a formula

$$X = b_0 + b_1 \cos \omega t + b_2 \cos 2 \omega t + b_3 \cos 3 \omega t + \dots$$

In other words when a periodic force of only one frequency is impressed upon the ear-drum this same frequency and in addition all its harmonic frequencies are impressed upon the fluid of the inner ear.

If two pure tones are impressed upon the ear then δp is given by

$$\delta p = p_1 \cos \omega_1 t + p_2 \cos \omega_2 t$$

If this value is substituted in equation (2), terms of the form $\cos^n \omega_1 t$ and $\cos^m \omega_2 t$ and $\cos^n \omega_1 t \cos^m \omega_2 t$ are obtained. The first two forms give rise to all the harmonics and the third form gives rise to the summation and difference tones. For example, the first four terms are

$$a_0 = a_0$$

$$a_1 \delta p = a_1 (p_1 \cos \omega_1 t + p_2 \cos \omega_2 t)$$

$$a_2 (\delta p)^2 = a_2 \left[\frac{1}{2} p_1^2 \cos 2 \omega_1 t + \frac{1}{2} p_2^2 \cos 2 \omega_2 t + p_1 p_2 \{ \cos (\omega_1 - \omega_2) t + \cos (\omega_1 + \omega_2) t \} + \frac{1}{2} (p_1^2 + p_2^2) \right]$$

$$\begin{aligned} a_3 (\delta p)^3 = a_3 & \left[\left(\frac{3}{4} p_1^3 + \frac{3}{2} p_1 p_2^2 \right) \cos \omega_1 t + \frac{1}{4} p_1^3 \cos 3 \omega_1 t + \right. \\ & \left(\frac{3}{4} p_2^3 + \frac{3}{2} p_1^2 p_2 \right) \cos \omega_2 t + \frac{1}{4} p_2^3 \cos 3 \omega_2 t + \frac{3}{4} p_1^2 p_2 \cos (\omega_2 t + 2 \omega_1 t) \\ & + \frac{3}{4} p_1^2 p_2 \cos (\omega_2 t - 2 \omega_1 t) + \frac{3}{4} p_1 p_2^2 \cos (\omega_1 t + 2 \omega_2 t) \\ & \left. + \frac{3}{4} p_1 p_2^2 \cos (\omega_1 t - 2 \omega_2 t) \right] \end{aligned}$$

Therefore unless there is a linear relation between a force acting on the ear-drum and the displacement at the oval window, that is unless all the coefficients in equation (2) are zero except a_1 , all the harmonics and the summation and difference tones will be impressed upon the fluid in the cochlea of the inner ear.

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New Method for the Disinfection of Hides and Skins for Anthrax.—Anthrax is an occupational disease of the tanning industry, the spores being carried by the hides and skins. The present methods for the disinfection of hides and skins for anthrax are not entirely satisfactory. HENRY FIELD SMYTH and EDWIN FREDERIC PIKE, of the University of Pennsylvania (*Amer. Jour. Hygiene*, 1923, iii, 224-237), have studied the disinfectant action of the following reagents upon anthrax spores: Chlorine, bromine, iodine, hydrochloric acid, carbonyl chloride (phosgene), carbon tetrachloride, trichloroethylene, sulphur dioxide, and ammonia. Experiments were also made on hides. The results obtained by Smyth and Pike demonstrate the absolute efficacy of iodine as a disinfectant for anthrax, and the possibility of the use of iodine for this purpose in the tanning industry without the slightest injury to the hides. The iodine may be applied as a vapor, as an aqueous solution, or in solution in an easily volatile solvent such as carbon tetrachloride or a mixture of that compound with gasoline.

J. S. H.

THE COEFFICIENT OF RECOMBINATION OF THE NATURAL IONS IN AIR, AND ALLIED PHENOMENA ASSOCIATED WITH WEAK ATMOSPHERIC IONIZATION.*

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I.

INTRODUCTION.

Earlier Methods and Results.—The equations governing the rate of increase of ions in a gas under the influence of a source of ionization producing q ions per c.c. per second, a coefficient of recombination α and a coefficient of diffusion D are

$$\begin{aligned}\frac{\partial n_+}{\partial t} &= D \frac{\partial^2 n_+}{\partial x^2} + q - \alpha n_+ n_- \\ \frac{\partial n_-}{\partial t} &= D \frac{\partial^2 n_-}{\partial x^2} + q - \alpha n_+ n_-\end{aligned}$$

Several methods have been devised for determining α , the aim being usually to arrange the experiment so that diffusion is negligible and $n_+ = n_-$, in which case

$$\frac{dn}{dt} = q - \alpha n^2. \quad (1)$$

If the source of ionization responsible for q is removed so that we obtain an equation which integrates to the form

$$\frac{1}{n} - \frac{1}{n_0} = \alpha t$$

we may obtain α by measuring the value of n at any instant t , and the value n_0 at the time $t = 0$ when the source is removed. In this form the equation was first used by J. J. Thomson and Rutherford,¹ the latter of whom² also investigated the truth of equation (1) as regards its form.

For the steady state, (1) gives

$$\alpha n^2 = q$$

* Communicated by Dr. W. F. G. Swann, Associate Editor of this JOURNAL.

¹ *Phil. Mag.*, 42, p. 392 (1896).

² *Phil. Mag.*, 44, p. 422 (1897), and 47, p. 109 (1899).

which serves to determine α in terms of q and the number of ions per c.c. in this state. McClung³ used this method.

The field intensity between two plates determines the time required to clear out the ions, and this time affects the loss by recombination. Langevin⁴ and Thirkill⁵ determined α from these losses under different field intensities.

Using the methods indicated above, and artificially produced ionization, various observers⁶ have obtained the following results: α increases as the temperature is lowered, and over considerable ranges is proportional to the pressure. For dust-free gases under normal conditions, α varies between 0.9×10^{-6} and 2.1×10^{-6} cm.³/sec. being for air about 1.6×10^{-6} . For atmospheric air (*i.e.*, some dust, moisture, etc., present) the value is about 4×10^{-6} .

Another important fact should be noted. Work done by Bragg and Kleeman,⁷ Langevin, Moulin,⁸ Wheelock,⁹ Ogden¹⁰ and Jaffé¹¹ has shown that when ions are produced in columns as in α -ray ionization, the recombination is more rapid than if the same number of ions were distributed uniformly throughout the ionization chamber. Plimpton¹² thus explained a high initial recombination obtained when using Röntgen rays, but in Part II it will be shown that the explanation in this case is open to question.

Recent Work.—In the work on recombination so far discussed the ions were produced by some strong local source which could be controlled. This will be called "artificial" ionization. No

³ *Phil. Mag.*, 3, p. 283 (1902).

⁴ Thèse, Paris, 1902, and *Ann. de Chim. et de Phys.*, 28, p. 433 (1903).

⁵ *Roy. Soc. Proc.*, 88, p. 477 (1913).

⁶ Schuster, *Manchester Soc.*, 48 (1904); Hendrin, *Phys. Rev.*, 21, p. 314 (1905); Retschinsky, *Ann. der Phys.*, 17, p. 518 (1905); Mache and Rimmer, *Phys. Zeits.*, 7, p. 617 (1906); Phillips, *Roy. Soc. Proc.*, 83, p. 246 (1910); Erikson, *Phil. Mag.*, 23, p. 747 (1912); Thirkill, *Roy. Soc. Proc.*, 88, p. 477 (1913); Plimpton, *Phil. Mag.*, 25, p. 65 (1913); Ogden, *Phil. Mag.*, 26, p. 991 (1913); Rümelin, *Ann. der Phys.*, 43, p. 821 (1914); Kohlrausch, *Sitz. der Wien. Ak.*, 123, p. 2321 (1914); Gockel, *Neue Denkschr. d. Schweiz Naturf. Gesellsch.*, 54, Abh. 1 (1917).

⁷ *Phil. Mag.*, 10, p. 318 (1905).

⁸ *Comptes Rendus*, 148, p. 1757 (1909), and Thèse, 1910.

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¹¹ *Ann. der Phys.*, 42, p. 303 (1913); *Phys. Zeits.*, 15, p. 353 (1914).

¹² *Phil. Mag.*, 25, p. 65 (1913).

attempts had been made to determine α , using the ever-present "natural" ionization. This was undertaken by the writer in 1916, using air which had been confined in the ionization chamber for some time. Other work made it necessary to leave the problem very soon after it was undertaken, but a preliminary unpublished value of about 1.6×10^{-6} was obtained.

Von Schweidler,¹³ in 1918 and 1919, assumed there was in ordinary air a loss of ions by collisions with dust, smoke particles or other matter, and so wrote

$$\frac{dn}{dt} = q - \alpha n^2 - \gamma nN \tag{2}$$

where N is the number per c.c. of these particles. This can be rewritten

$$\frac{dn}{dt} = q - \alpha n^2 - \beta n = q - n^2 \left(\alpha + \frac{\beta}{n} \right) = q - \alpha' n^2$$

Results of experiments extending over a month gave values of α' varying between 9×10^{-6} and 115×10^{-6} with a mean value of 29×10^{-6} for outdoor air.

In view of these large values he wrote the steady state equation

$$q = \alpha n^2 + \beta n = n (\alpha n + \beta) = \beta' n.$$

The results of his earlier and later work may be summed up as follows:

TABLE I.

q	n	$\beta' \times 10^3$	Extremes, $\times 10^3$	Remarks.
26.11	1200	21.8	16 to 60	Innsbruck, well-ventilated room.
17.6	1080	16.6	12 to 42	Seeham, well-ventilated room.
13.6	712	19.1	16 to 35	Seeham, wooden house over the water.
29.5	740	42.2	18 to 98	Innsbruck, closed heated room.

In connection with the last observations he found that β' was independent of q even when the latter was increased by use of a mesothorium capsule to a value as high as 347 ions per c.c. per second.

Owing to the interruption of communications due to the war, the investigations here presented were undertaken without knowledge of Schweidler's work. There are so many phases of the

¹³ *Akad. Wiss. Wien. Ber.*, **127** (2a), p. 953 (1918); *Akad. Wiss. Wien. Ber.*, **128** (2a), p. 947 (1919).
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general subject, however, which did not come within the scope of his discussion or investigation that it was found possible to continue the present work without serious duplication of effort. His method of observation was found to be very similar to that employed in the preliminary work in 1916.

One of the outstanding features of Schweidler's results is the fact that the absorption particles in atmospheric air do not appear to be dust particles in the ordinary sense of the word, since β' remains fairly constant for wide variations in dust content. One of the main objects of the present investigation and of that made by the writer in 1916 was to determine whether, apart from the influence of dust, the mechanism of recombination for such weak ionization as occurs in the atmosphere is essentially different from that for the strong ionization usually employed in the laboratory. This question is of primary importance in determining how far it is justifiable to apply previous laboratory results to atmospheric phenomena.

METHODS OF MEASUREMENT.

The determination of α as first carried out involved the determination of q and n_∞ in the relation $q = \alpha n_\infty^2$, corresponding to the steady state.

The most obvious method of determining q is to measure the saturation current through the vessel, and make the necessary calculation in terms of the volume, and the electronic charge. Another method is founded upon the following principle. Without any assumption as to the law of recombination we can write for the non-steady state,

$$\frac{dn}{dt} = q - f(n)$$

where all that we need specify concerning $f(n)$ is that it is zero when n is zero. Thus the initial rate of growth of ions immediately after the vessel has been cleared of ions by a strong field, affords a direct measure of q .

The latter method has some advantages over the former, in that even though there is initial columnar recombination, the value of q measured in this way gives what we may regard as the true rate at which ions are supplied to the space, and it is therefore the appropriate value to use in a calculation of α from the formula $q = \alpha n_\infty^2$, which takes no account of initial recombination. The

value of q obtained from the saturation current would, on account of the high field used in measuring the current, include a part of the ionization which, in the absence of that field, would participate in the initial recombination. For the purpose of obtaining an estimate of the extent of this initial recombination, both methods of measuring q were employed.

There are two obvious ways of measuring n_{∞} . In the first, which was the one usually employed, the ions existing in the vessel in the steady state were swept out by the application of a high electric field. If Q is the quantity of electricity delivered to the insulated system under these conditions, after correction for the formation and recombination of ions during the process of sweeping them out, we may obtain n_{∞} in terms of the electronic charge e and the volume V of the vessel by the relation $Q = n_{\infty} e V$.

The second method involves the measurement of the steady current obtained when between the electrodes is maintained a difference of potential which is so small that, except in the immediate vicinity of the electrodes, the value of n within the vessel is not appreciably disturbed from the value n_{∞} by the passage of the current. Under these conditions, if Q_0 is the charge contained within any closed surface surrounding the central conductor, the current i coming to that surface is

$$i = -4\pi Q_0 n e (v_+ + v_-)$$

where v_+ and v_- are the mobilities of the positive and negative ions. The closed surface referred to must not be drawn so near the inner conductor that any part of it falls within the region in which n_+ and n_- vary. Thus Q_0 is not the actual charge on the central conductor. The relationship of these two quantities raises considerations concerning the very meaning of the capacity of such a system as is here considered. This question has an importance far beyond its bearing on the immediate problem of the coefficient of recombination of ions, and will be given careful consideration in Part II. As far as the present problem is concerned, it may be stated that the two methods indicated for determining n_{∞} gave concordant results.

MATHEMATICAL FORMULAS AND CORRECTIONS.

It will be well at this point to consider the corrections which must be made to the Q from which n_{∞} is obtained by the first method indicated above.

(a) For an approximate correction, the Q originally obtained should be diminished by a quantity equal to the saturation current for the time interval during which the observation lasts.

(b) After applying correction (a), we must increase Q to account for recombination during the interval of observation. If we assume a parallel plate condenser and that when the potential is applied all ions move toward the plates with the same velocity, then the region in which practically the whole recombination takes place is one which is symmetrical with respect to a plane equidistant from the plates, and which becomes zero after a time $T/2$, where T is the time required for an ion to travel the whole distance between the plates. The volume of this region at any time t after the potential is applied can be expressed by $V = V_0(1 - 2t/T)$ where V_0 is the volume of the vessel. The total number recombining in this region is

$$N = V_0 \alpha n_\infty^2 \int_0^{T/2} \left(1 - \frac{2t}{T}\right) dt$$

and since $\alpha n_\infty^2 = q$ the solution becomes

$$N = V_0 q T/4.$$

It is easy to apply a potential sufficiently high to make $T = 2$ seconds, and if we assume $q = 10$ ions per c.c. per second and $n = 1000$ ions per c.c., we obtain for the loss $N/V_0 n_\infty = 0.5$ per cent.

(c) At the end of the experiment there are still ions in the vessel. If we let d be the total distance between the plates and measure x from one of the plates, we have $n = q T x/d$, and the total number of ions of this class becomes $V_0 q T/2$. This correction to n_∞ is therefore about 1 per cent.

(d) The correction which presents the greatest difficulty is that for diffusion. During the progress of the work the solutions of three different differential equations involving diffusion were required. They were obtained as follows:

(1) The steady state equation

$$D \frac{d^2 n}{dx^2} + q - \alpha n^2 = 0$$

may be integrated once and obtained in the form

$$\frac{dn}{dx} = \left(\frac{2\alpha}{3D}\right)^{\frac{1}{2}} \left(n^3 - \frac{3qn}{\alpha} - \frac{3a}{\alpha}\right)^{\frac{1}{2}}$$

where a is the constant of integration.

For a parallel plate condenser, if the plates are an infinite distance apart, at a great distance from either plate, n becomes n_∞ , $q = \alpha n_\infty^2$, and $\frac{dn}{dx} = 0$. This gives $a = -2\alpha n_\infty^3/3$.

Substituting this value of a , putting αn_∞^2 for q and separating the variables, we obtain upon integrating

$$\begin{aligned} \left(\frac{2\alpha n_\infty}{3D}\right)^{\frac{1}{2}} x &= \int_0^{\frac{n}{n_\infty}} \frac{d\left(\frac{n}{n_\infty}\right)}{\left[\left(\frac{n}{n_\infty}\right)^3 - 3\frac{n}{n_\infty} + 2\right]^{\frac{1}{2}}} \\ &= \frac{1}{\sqrt{3}} \log \left[\frac{\sqrt{\frac{n}{n_\infty} + 2} - \sqrt{3}}{\sqrt{\frac{n}{n_\infty} + 2} + \sqrt{3}} \cdot \frac{\sqrt{2} + \sqrt{3}}{\sqrt{2} - \sqrt{3}} \right] \end{aligned}$$

where x is the distance from the plate.

In Table II are given corresponding values of n/n_∞ and x (in row x_α), assuming that $D = 0.04$ cm.²/sec. and $\alpha n_\infty = 8 \times 10^{-3}$.

Making the assumption that the first ionization chamber used could be treated as a parallel plate condenser with plates 12.6 cms. apart and containing the same volume as the ionization chamber, and making the further assumption that the total number of ions lost by diffusion would be no greater even if the plates were an infinite distance apart, the loss is found by graphical integration to be 29 per cent.

(2) Using the boundary conditions that $n/n_\infty = 0$ when $x = 0$, the solution of the steady state equation

$$D \frac{d^2 n}{dx^2} + q - \beta n = 0$$

was obtained in the form

$$\frac{n}{n_\infty} = 1 - e^{-\sqrt{\frac{\beta}{D}} x}.$$

In Table II are included corresponding values of n/n_∞ and x (in row headed x_β) obtained from this equation. Again $D = 0.04$ and $\beta = 8 \times 10^{-3}$. This is the value of αn_∞ used previously and so the resulting values of x may be compared directly. Making the assumptions used in the previous case, the diffusion loss is found to be 36 per cent.

TABLE II.

$\frac{n}{n_\infty}$	0	0.2	0.4	0.6	0.8	0.9	0.95	0.97	0.99	0.995
x_α cms.	0	0.42	0.94	1.65	2.81	3.94	5.06	5.88	7.74	10.62
x_β cms.	0	0.51	1.12	2.03	3.56	5.08	6.74	7.76	10.5	13.0

(3) The non-steady state equation

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} + q - \beta n$$

was solved as follows for the boundary conditions:

$n = 0$ when $t = 0$ for all values of x ,

$n = 0$ when $x = 0$ for all values of t .

By making the substitution $n = N + q/\beta$, the equation reduces to the form treated in Byerly "Fourier Series and Spherical Harmonics" (page 90), and two particular solutions there given can be added to secure the boundary conditions desired in the present problem. Remembering that $q/\beta = n_\infty$ and replacing N by $n - q/\beta$ the solution may be written

$$\frac{n}{n_\infty} = 1 - \frac{2e^{-\beta t}}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy - \frac{2}{\sqrt{\pi}} \int_{\frac{x}{2\sqrt{Dt}}}^\infty e^{-y^2 - \frac{\beta x^2}{4Dy^2}} dy$$

This equation can be integrated with respect to x and obtained in the form

$$\begin{aligned} \frac{1}{n_\infty} \int_0^\eta n dx &= \eta - \frac{2\eta}{\pi} e^{-\beta t} \int_0^{\frac{\eta}{2\sqrt{Dt}}} e^{-y^2} dy \\ &- 2\sqrt{\frac{Dt}{\pi}} e^{-\beta t} \left(e^{-\frac{\eta^2}{4Dt}} - 1 \right) - \sqrt{\frac{D}{\beta}} \sinh \eta \sqrt{\frac{\beta}{D}} \\ &+ \sqrt{\frac{D}{\pi\beta}} \left[e^{\eta\sqrt{\frac{\beta}{D}}} \int_0^{\frac{\eta}{2\sqrt{Dt}} + \sqrt{\beta t}} e^{-y^2} dy \right. \\ &\left. - e^{-\eta\sqrt{\frac{\beta}{D}}} \int_0^{\frac{\eta}{2\sqrt{Dt}} - \sqrt{\beta t}} e^{-y^2} dy - 2 \int_0^{\sqrt{\beta t}} e^{-y^2} dy \right] \end{aligned}$$

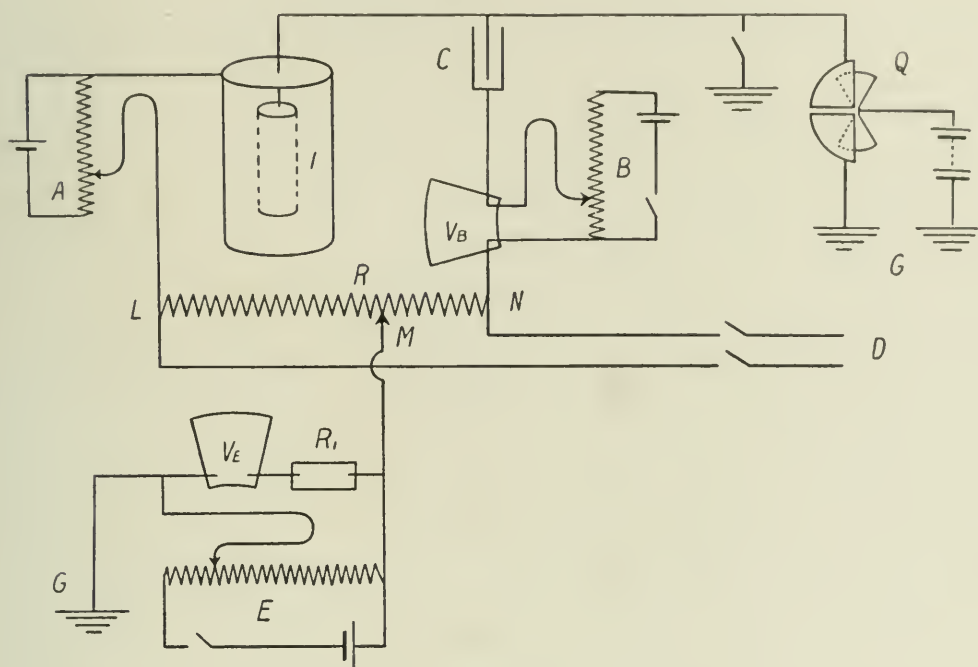
where η is half the distance between the plates. Having fixed D and β this can be immediately evaluated for any desired value of t . Dividing by η gives the average value of n/n_∞ at the time t .

In the absence of diffusion the solution of the non-steady state equation may be written

$$\frac{n_d}{n_\infty} = 1 - e^{-\beta t}$$

where n_d indicates the value of n in the absence of diffusion. From n/n_∞ and n_d/n_∞ a value of n/n_d may be obtained and any measured value of n corrected for diffusion. Using the values of

FIG. 1.



η , D and β , indicated previously, the results in Table III were obtained.

TABLE III.

Time in minutes.	∞	5	4	3.5	3	2.5	2	1.5	1	0.75	0.50	0.25
$\frac{n}{n_d}$	0.667	0.692	0.704	0.714	0.733	0.742	0.764	0.793	0.825	0.847	0.880	0.897

DESCRIPTION OF APPARATUS AND MANIPULATION.

During the progress of the investigation, ionization chambers of various sizes and forms were used, also the arrangement of apparatus and method of observation were varied to meet immediate requirements, but the arrangement used for the greater part of the work is indicated in Fig. 1.

The insulated electrode of the ionization chamber I was connected to one pair of quadrants of an electrometer Q whose

sensitivity varied in different experiments from 300 to 6000 divisions per volt. To prevent leakage from the outer wall of the ionization chamber to the central system, the latter was protected by an earthed guard ring. The potentiometer system A served to neutralize any contact difference of potential between the outer wall and the central cylinder. The potentiometer system B , in connection with the variable condenser C , served for calibration purposes. For most of the work, V_B was a standard millivoltmeter. The lead wires of the central system were carefully shielded by metal tubing. In order to avoid trouble resulting from the inductive action arising from variation of the potential of the batteries during the measurement of q , and for the further purpose of rendering it possible in the determination of n suddenly to apply a potential to the outer vessel with the electrometer system insulated and yet obtain no inductive deflection, the scheme of compensation devised by Swann was employed.¹⁴ The leads from the battery were brought *via* D to the two ends of the resistance R , which was composed of coils of $IAIA$ wire immersed in oil and wound to a total resistance of 30,000 ohms. If the potential of M is kept equal to zero or any definite value, it is possible to adjust the capacity C so that complete compensation is secured as regards the potential of the electrometer system when the battery D is thrown off or on. Moreover, by varying the potential of the point M by means of the potentiometer system E , it is possible to annul the change of potential of the electrometer system arising from the advent to that system of the charges which it is desired to measure, so that the magnitudes of these charges are obtained in terms of the readings of the millivoltmeter V_E , being in fact KV_E , where K is a constant. The sensitivity of V_E is varied at will by the series resistance R_1 . In order to determine K the central system is first earthed, the switches in the circuits B and E are closed, and by trial the sliding contacts on the resistances are so set that upon releasing the electrometer from earth and then opening the two switches the electrometer does not deflect. The voltmeter reading V_E under these conditions indicates a quantity of electricity on the central system equal to $C \times V_B$. The inverse of this method of calibration may lead to error, for as soon as the point M (also L and N) is at a potential other than

¹⁴ *Phys. Rev.*, **17**, p. 240 (1921).

zero, this potential is applied to the outer wall of the ionization chamber and an ionic current results. Under the conditions above, $KV_E = CV_B$, which serves to determine K in terms of C and the measured potentials. The advantage of using the system E rather than B during the main measurements is that, during these measurements, the whole of the system B is at a potential appreciably different from zero, so that it is not desirable to handle it for the purpose of making adjustments.

All parts of the entire system except the batteries at D were carefully insulated from the ground, in fact the indicated "grounds" G were also carefully insulated from the actual ground, being merely connected at a common point. The purpose of this was to prevent leakage from the high potential batteries to any part of the system, as variable shunts across the high resistances would cause the voltages to fluctuate.

FIRST OBSERVATIONS AND RESULTS.

The first observations were made to verify the work done in 1916, no especial effort being made to purify the air. The ionization chamber consisted of coaxial sheet iron cylinders, the outer about 65 cms. in length and 43 cms. in diameter, the inner 40 cms. in length and 18 cms. in diameter. The effective volume was taken as 8.40×10^4 c.c. Tests indicated that 280 volts across the resistance R was sufficient to secure saturation; about half of this was across the ionization chamber. Test also showed that seven minutes were sufficient time for the ionization very nearly to reach its normal state; eight to ten minutes were usually allowed. Before taking observations the potentiometer A was so adjusted that with the high potential off there was no drift of the electrometer when released. The potential required to secure no drift did not remain exactly the same from day to day, but was always small. Next the system was balanced, *i.e.*, the capacity C and the resistances of R were so adjusted that removing the high potential produced no deflection of the electrometer.

In taking observations, the electrometer was released, the high potential applied and the electrometer held at its zero reading by increasing the potential V_E . After 30 seconds V_E was noted, and then at various other intervals of time afterward. The latter observations gave data for obtaining q , while the value of n_∞ was obtained from the first observation. The 30-second time interval allowed any initial electrometer oscillations to die out.

Besides the observations made with natural ionization, observations were made with radium bromide near the vessel. The results of these first observations may be seen in Table IV.

TABLE IV.

q		n_{∞}		$\alpha \times 10^6$	
+	-	+	-	+	-
14.35	14.2	2470	2580	2.4	2.1
14.6	14.3	2990	2820	1.6	1.8
17.15	17.35	3000	2720	1.9	2.3
17.2	17.7	3460	3130	1.4	1.8
20.4	20.8	3510	3230	1.7	2.0
38.3	38.5	5880	5470	1.1	1.3
63.6	64.8	6560	6130	1.5	1.7

The only corrections applied to n_{∞} in the table are those discussed under (a) and (1) of (d). It is realized that the latter correction is only an approximation owing to the assumptions involved.

The values of α determined from measurements on negative ions appear in general to be greater than for the positive ions. This may be due to the greater loss of negative ions by diffusion.

RESULTS AFTER MODIFYING APPARATUS.

In order to minimize the uncertainty due to diffusion, measurements were made in a large cylindrical vessel whose effective volume was estimated to be 2.06×10^6 c.c. With this apparatus values of α as high as 100×10^{-6} were obtained, this resulting from $q = 23.6$ and $n = 486$, after adding a correction of 6 per cent. for loss by diffusion calculated in the same manner as before.

Investigations were immediately undertaken to determine the cause of these high values. To determine their reality, q and n_{∞} were each measured by the two different methods indicated previously. The values of n were in agreement, those of q differed slightly, as is shown in Table VII, but the difference was not nearly sufficient to account for the large values of α obtained. A discussion of columnar ionization and its effect on the measured q will be given later, and the results obtained will there be considered.

The possibility was next considered of accounting for the large values of α on the basis of equation (2) as proposed by Schweidler. Various subsidiary experiments were made in this

connection, but a discussion of these matters will be postponed until after a method of determining α and β has been indicated and the results of measurements given.

TESTING OF n - t CURVES.

General Method.—The following procedure was adopted in determining values of q , α and β for the non-steady state equation

$$\frac{\partial n}{\partial t} = q + D \frac{\partial^2 n}{\partial x^2} - \alpha n^2 - \beta n.$$

Relying for justification upon results obtained, it is assumed that the αn^2 term is negligible in comparison with βn . The equation then reduces to one whose solution has been given, and by use of Table III the measured values of n obtained for various time intervals may be corrected for diffusion. A curve constructed from these values of n and t should then satisfy the equation

$$\frac{dn}{dt} = q - \beta n$$

whose solution, using the boundary condition $n = 0$ when $t = 0$, is

$$n = \frac{q}{\beta} (1 - e^{-\beta t}).$$

Various values of t were substituted in this equation and the values of q and β adjusted until the computed values of n agreed as well as possible with those taken from the corrected experimental curve.

Typical Set of Data.—A typical set of data will now be given and the results of the adjustment shown. The original ionization chamber was used in this work so that the purity of the air could be better controlled. The potential across the ionization chamber was about 400 volts and the time required for the observations was about three hours.

The figures recorded in Table V are the scale indications of the voltmeter V_E . The ions were allowed two hours to reach a steady state before commencing observations, then the last reading in the second column of the table was taken. A test for balance then showed that 2.2 should be added to the observed reading. The system was then balanced so that no further corrections of this kind were necessary. Next the data in the first line of the table were taken. This was followed by the data in column 2, then in columns 3, 4 and 5, and finally by the data in the second line of the table. The sixth column gives the average of the preceding

four. From this average is subtracted 10.72 to correct for ions formed during the experiment, and 0.6 is added for zero correction on the voltmeter. The corrected values appear in column seven, and these were converted into the values of n appearing in the next column by use of the following calibration data.

The charge resulting from a potential of 0.300 volt on the condenser C of capacity 68.5 cms., balanced the charge induced by the potential corresponding to a reading of 41.4 divisions on the voltmeter, giving the value 0.001631 e.s.u. of quantity per division, or 40.5 ions per c.c. per division, taking the volume as 8.40×10^4 c.c. and the ionic charge as 4.8×10^{-10} e.s.u. From the saturation current, q was found to be 14.5 ions per c.c. per second. The values of n_d were obtained from n by use of Table III.

TABLE V.

March 20, 1921.

q current in two minutes

0 to 42.1, 44.1, 42.7, 43.0, 42.0,
41.0, 42.6, 42.7, 43.5, 44.2.

Average q current in 30 seconds, 10.72.

Time for ions to form.	Voltmeter reading 30 seconds after throwing on potential.				Average.	Corrected for q and zero.	n	n_d
15 sec.	12.7	14.5	13.5	14.6	13.82	3.70	150	167
30	16.8	17.1	18.7	17.1	17.42	7.30	296	337
45	20.2	19.1	21.0	20.1	20.10	9.98	404	477
1 min.	21.9	22.4	23.9	23.2	22.85	12.73	516	626
1.5	28.2	28.0	27.6	28.3	28.02	17.90	725	914
2	29.8	30.2	31.0	30.9	30.48	20.36	825	1080
2.5	33.0	34.0	33.0	32.2	33.05	22.93	929	1250
3	35.3	37.1	36.4	35.5	36.08	25.96	1050	1434
3.5	38.8	38.4	36.7	36.4	37.58	27.46	1112	1560
4	39.5	39.0	39.0	38.8	39.08	28.96	1172	1666
2 hrs.	41.6	corrected for balance gives			43.8	33.7	1365	2070 $= n_\infty$

A curve $n_d - t$ was next plotted, and from this was taken the values of n_d and t given in the first two rows of Table VI. The third row gives the values computed for n , assuming $\alpha = 0$, $\beta = 4.6 \times 10^{-3}$, $q = 11.7$, using the equation $n = (1 - e^{-\beta t})q/\beta$. The agreement of the two values of n was considered good.

The value of β obtained is only about half that used in determining the diffusion corrections in Table III. Computed values of n_d , using this smaller value of β , are shown in the last line of

the table, and it is seen that even this change in β has relatively small effect upon the diffusion correction.

TABLE VI.

t (sec.)	18	37	58.5	81	106.5	139	174	220.5
n_d ($\beta = 8 \times 10^{-3}$)	200	400	600	800	1000	1200	1400	1600
n	203	396	599	790	983	1201	1400	1617
n_d ($\beta = 4.6 \times 10^{-3}$)	208	428	630	828	1205	1240	1436	1644

Results.—Twenty-four curves were obtained and tested in this way, assuming $\alpha = 0$, and the results are indicated in Table VII, in the columns headed "Tests of curves after correcting for diffusion." The column headed " R " indicates the percentages obtained by dividing the largest variation of n by the largest value of n used. The smallness of these variations is a measure of the justification of neglecting the αn^2 term in this work. Where no value of β accompanies that of q , the q was obtained from the initial slope of the curve.

The following remarks are supplementary to those appearing in Table VII. On January 28th, the vessel was filled with air, which was slowly filtered through cotton for a period of over two hours, and was obtained from a high-pressure cylinder which had been filled over a month previously so as to permit the decay of possible radium emanation content. On February 3rd, a small amount of radium emanation was introduced into the vessel without disturbing materially the conditions inside. On March 8th, the vessel was cleaned inside and a coating of glycerin applied, which, together with a small fan inside, aided in removing dust particles. On March 19th, the vessel was again cleaned, covered with glycerin, sealed as well as possible with cotton wool, and a dish of phosphorous pentoxide placed inside.

The data for the second curve on March 2nd was taken shortly after room air had been pumped into the vessel, and the original observations show that for any given value of t , the measured n was continually increasing, thus making it difficult to secure a good set of observations. For some of the curves the value of n corresponding to a given t depends upon only one or two observations, and the resulting inaccuracy in drawing the curve is thought to explain most of the two and three per cent. variations.

As a check on the values of β obtained from curve testing, β

was computed from the equation $\beta = q_c/n_\infty$, where q_c is the value of q obtained from curve testing and n_∞ is taken from the first

TABLE VII.

Date— 1921.	n_∞ cor- rected for dif- fusion.	q from satura- tion cur- rent.	a $(=\frac{q}{n_\infty^2})$	β $(=\frac{q_c}{n_\infty})$	Test of curves after correcting for diffusion.			Remarks.
					q_c	β	R Per cent.	
Jan. 19	2,040	12.6	3.0×10^{-6}	5.6×10^{-3}	11.4	5.0	1.2	Room air in Jan. 18.
20	1,470	11.7	5.4		10.2			
20	1,780	12.6	4.0	6.1	10.8	4.0	0.6	
20		12.45			8.4			
23	1,930	12.2	3.3					Natural ionization. Radium bromide. Filtered air.*
23	4,560	35.6	1.7	8.3	39.9	8.0	0.6	
28	1,470	9.7	4.5					
28	1,580	9.8	3.9	5.6	8.92	4.0	1.0	
30	1,480	10.5	4.8		8			Radium bromide.
30	1,480	10.4	4.7	6.7	9.9	5.7	0.8	
30								
30	4,070	30.3	1.8	7.9	32.2	7.0	1.1	
Feb. 2	6,140	58.5	1.6	9.6	59.1	8.0	1.7	Radium bromide.
3	1,720	12.2	4.1					
3		12.2			9.5			
3	2,300	20.1	3.8					
3	2,270	21.0	4.1					Emanation intro- duced.
3		21.8			19.6	9.5	1.0	
3	2,530	23.0	3.6	8.0	20.3	7.0	0.8	
3	2,670	22.8	3.2		17			
3	4,390	39.6	2.1	9.7	38.5	7.0	2.5	Radium bromide.
3	2,720	23.6	3.2		14			
4	2,130	21.0	4.6					
4		20.7			15			
5	1,970	17.9	4.6		16			Radium bromide.
5		44.7			38			
12	1,590	13.2	5.2	9				
12	3,640	31.0	2.3	7.9	28.8	5.3	1.2	
12	17,400	386	1.3	21	361	10	3.4	Radium bromide.
20	17,500	400	1.3	26	451	22	1.2	Radium bromide.
23	3,490	32.7	2.7	8.5	29.5	5.5	1.2	Radium bromide.
23		24.1			22.0	5.5	2.5	Radium bromide.
23		13.5			12.5	6.8	1.2	
27		13.0			11.2	6.5	1.9	
Mar. 2	1,640	13.3	4.9	6.5	10.9	5.2	1.5	Smoke in Feb. 27.
2		14.7			13.9	17	5.5	Room air pumped in.
12		11.6			10.5	5.3	2.2	Air in Mar. 8.
13	1,580	11.3	4.5	6.8	10.8	6.3	1.5	
20	1,930	14.5	3.9	6.1	11.7	4.6	1.1	Air in Mar. 19 with phos. pentoxide and glycerin.
25		18.8			16.1	6.0	1.1	
29	1,880	17.8	5.0	7.7	14.4	6.6	1.1	

*Introduced about four hours before.

column. These values of β should be given less weight, as each usually depends upon a single measurement of n_∞ , while those

obtained from curve testing depend upon several measurements of n .

Tests were made to see if it were possible by a suitable choice of q and α to fit the experimental curves without the use of a β term. Using data taken soon after the introduction of radium emanation as being most favorable, but restricting q to values in the neighborhood of those obtained by experiment, the values of R obtained were of the order 30 per cent. Tests of other curves gave very similar results, thus showing the use of a β term to be necessary.

It is seen that the values of β vary over a comparatively small range, averaging 6.1×10^{-3} if the three large values obtained under unusual conditions are eliminated. In practically all cases the air had stood for some time. For fresh air where the dust has had little opportunity to settle, larger values would be expected as will be seen later, and as were actually found by Schweidler.

As a result of the curve testing, the conclusion seems justified that under the conditions existing during the observations the recombination due to the αn^2 term is negligible in comparison with that due to βn . This confirms Schweidler's conclusion that it is more appropriate to determine a coefficient of recombination depending upon the first power of the number of ions than one depending upon the square of this number. As pointed out previously, Schweidler decided that the absorption centres were not dust particles in the ordinary sense of the word. We now find that the β term predominates under a wide variety of conditions involving variation in the sources and degree of ionization, and different degrees of purity of the air, and that the n^2 term is still negligible even when special care is taken to entirely remove dust and moisture.

This shows that it is not justifiable to take the recombination coefficients obtained in the laboratory by methods using strong artificial ionization and apply them to natural ionization phenomena. The phenomena are quite distinct, possibly due to a non-uniform distribution of ions in the case of natural ionization. A recombination depending upon the first power of n may be accounted for on this basis as follows: Suppose the ionization and recombination to be confined to small isolated regions which are quite similar in nature. Then no matter what the law of recombination may be in each individual region, the total recombination

is proportional to the number of regions, that is to the number of ions, and any increase in the ionization which merely adds more regions of a similar nature will leave the proportionality factor unchanged. As soon as the regions begin to overlap, more rapid recombination would be expected.

It is hoped that it will later be possible to carry this part of the work further, using a vessel large enough and of such shape that either diffusion can be neglected entirely or at least quite accurate corrections can be applied, and that the construction shall be such that the content of the air can be carefully controlled. If in addition provision can be made for varying the intensity of ionization up to values ordinarily used in laboratory experiments, it should be possible to study the conditions under which the term βn is gradually replaced in importance by αn^2 .

II.

In connection with the work presented in Section I, various matters came up for consideration and investigation which it seems advisable to present in a separate section, although closely connected with the previous work.

COLUMNAR IONIZATION.

The values taken for q and n_∞ are determined on the assumption that they are uniform throughout the vessel. This requires some consideration. Let us consider the conditions inside a cubical vessel having edges of 30 cms. and a total ionization of 10 ions per c.c. per second, 2.3 being due to α rays, the remainder to β and γ rays. Since one α particle produces about 2×10^5 pairs of ions, an emission of one particle every three seconds is all that is required, and all this ionization is confined to a narrow path about 5 cms. in length. If we assume all the remaining ionization to be due to β particles, that each has a range of 250 cms. and forms 75 pairs of ions per cm. of path, a computation shows that this ionization could be accounted for by β tracks spaced in rows and columns 3.1 cms. apart and running parallel to each other between opposite faces of the cube. The ionization due to γ rays is probably quite uniform but is small in amount.

Jaffé,¹⁵ in his theory of columnar ionization, gives an equation connecting the number of pairs of ions produced per unit length of column and the number still uncombined at any later instant.

¹⁵ *Loc. cit.*

Uncertainty as to the original radius of a column makes it difficult to evaluate, but by setting maximum and minimum limits, it appears that in the case of α tracks it is safe to assume that at least half the ions recombine within one second, while for β tracks there is very little recombination in this interval, or even in much larger intervals of time, and consequently, if the theory applies at all to β tracks, it indicates practically no columnar recombination. Another argument in favor of this conclusion is that if the effect were appreciable for β tracks it would be enormous for α tracks, and this is not the case. It is for these reasons that Plimpton's explanation of his results, as mentioned in the introduction, is considered unsatisfactory.

In view of the facts presented it is evident that the α -ray ionization is far from uniform. That due to β particles is possibly fairly uniform, the columns considered are rather far apart, but there is little columnar recombination and so the ions produced in successive seconds persist for some time.

Table VII includes values of q obtained from the saturation current and also from the initial slope of the corrected $n-t$ curves. A potential of about 400 volts was applied across the chamber. For natural ionization the small difference between the two values of q can be explained on the basis of initial recombination, since the total ionization due to α particles is about 2.3 for fresh outdoor air and less for older air.

About 90 per cent. of the additional ionization produced when radium emanation is introduced into the vessel should be due ¹⁶ to α particles. Consequently the increase in q , as obtained from the curves, should be considerably less than that obtained from the saturation current. The increase obtained from the curves was larger than expected, although possibly not unreasonably so.

Additional ionization produced by radium bromide is due to β and γ rays and so should manifest no effect of columnar ionization. The data seem in general to bear this out.

ABSORPTION CENTRES.

A number of questions arose in connection with the consideration of absorption centres, and several subsidiary experiments were carried out. Some of these matters will now be presented.

Number of Absorption Centres Necessary to Account for the

¹⁶ Rutherford, "Radioactive Substances and Their Radiations," p. 581.

β Term.—Assuming that the β term is due to collisions of ions with dust or other particles having negligible velocity, a rough determination on the basis of the dynamical theory of gases shows that 1000 particles per c.c. of radius 8×10^{-6} cm., or 10 of radius 8×10^{-5} cm., or 1 of radius 2×10^{-4} cm. would be sufficient to account for observed values of β . If it were permissible to explain the β term as indicated, it is seen that the number of particles necessary is not excessive. Where the particles are small, having radius 4×10^{-6} cm., for instance, a computation using Stokes' equation shows that the particles would fall only about 6 cms. per day in still air.

Experiments to Determine the Effect upon Recombination Due to the Presence or Absence of Nuclei.—It was found that artificial rain in the ionization chamber, the introduction of smoke, and of live steam, all produced very similar effects. The original purpose in sprinkling the air was to remove dust particles, but evidently great numbers of water particles remained suspended. An attempt was made to remove dust particles by introducing superheated steam, but it appears that the steam became sufficiently supersaturated by cooling to condense upon the ions as well, and remain suspended. Owing to the similarity of results, it is necessary to present only the results obtained by introducing smoke.

A strong jet of smoke was blown into the small galvanized iron vessel for 10 to 15 seconds. Calling the normal current strength unity, the current after introducing the smoke was over 20, but dropped to about 10 after twenty minutes. The potential was then taken off for fifteen minutes. When again applied, the initial current was about 12, diminishing to 6 after ten minutes. After another fifteen-minute wait with the potential off, the current was about 8, diminishing to 5 after five minutes. After an eight-minute wait the current was 7, reaching the fairly constant value of 3 after about twenty minutes.

Several hours later an attempt was made to obtain an n - t curve. It was found that n reached its maximum value in about thirty seconds, and the value was exceedingly low, being roughly 200 ions per c.c. About twenty-eight hours after this, a curve much nearer normal was obtained.

A small puff of smoke was again introduced, and again there

was practically no building up of ions. Air was then pumped through the chamber with a foot bellows, tests of n being made after every few minutes, and after about thirty minutes of pumping there was apparent a small growth in n . After standing for fifteen hours the ionization was very much greater, and after another nine hours it was slightly greater than its value just before the second puff of smoke was introduced. Two days later it was still about the same, n_{∞} being 1162 and q , 13.3. Room air was then pumped through the vessel for about three minutes and had the effect of increasing q by 10 or 15 per cent. and decreasing n about 35 per cent.

Explanation of Results.—Eve¹⁷ has shown that introducing smoke has the effect of producing a great number of large slowly moving ions, which owing to their slow motion are not detected in ordinary observations. The large initial current observed above upon introducing smoke was probably due to the gradual clearing out of some of these large ions and so was not a true saturation current. The rapidity with which this current decreased in magnitude would depend upon the mobility of the ions. An increased current after the potential had been removed for a time would be expected, as opportunity was thus given for the small ions to attach themselves to smoke particles instead of being drawn to the walls of the vessel immediately upon formation.

The inability to measure an n in the vessel by the ordinary method is probably due to the rapidity with which the small ions unite with the smoke particles. As the number of smoke particles decreases an increase in the measured n would be expected. This is probably the explanation of the increase of the measured n with time, the smoke particles gradually settling. Pumping air through the vessel would remove some of the smoke particles and this would produce an apparent increase in n , as was found. The decrease in n , found in the case where the vessel had been allowed to stand for some time and then air pumped in, was probably due to the introduction of more dust or smoke than was removed.

After the experiments indicated above, the vessel and insulation were carefully cleaned and dried, the inside covered with glycerin and a large tray of phosphorous pentoxide placed in the bottom. A small fan aided in producing circulation to remove

¹⁷ *Phil. Mag.*, 19, p. 657 (1910).

dust and moisture. The ionization was first tested before running the fan and even after seven hours the values of n obtained were very low. The fan was then run for about eighteen hours and a considerable increase in the apparent n resulted, the data in Table VII, under date of March 20th, showing the results obtained. The fan ran an additional thirty-seven hours before the observations on the 25th, and twenty-four hours more just previous to the observations on the 29th.

THE EFFECT OF IONIZATION UPON CAPACITY.

We will now consider the relationship between what may be called the "low potential capacity" and the ordinary or high potential capacity of an ionized gas condenser having plates some distance apart. This matter was merely referred to in Section I under "Methods of Measurement."

It was first shown by J. Zeleny¹⁸ that if two plates are placed in an ionized gas and a potential difference established, the field between is stronger in the neighborhood of the plates than at the centre. Thomson¹⁹ discussed the matter for the case where the plates were an infinite distance apart, and Swann²⁰ extended the calculations to plates at a finite distance. The result is obtained that the ratio of the field at the plates to that at the centre may, for natural ionization in air, reach a maximum value of 2.7²¹ for very small applied potentials. For larger potentials the ratio becomes less, approaching unity for fields sufficiently strong to clear out all the ions. It is easily shown that this ratio represents the ratio of the two capacities mentioned above.

Suppose a potential V to be applied across a parallel plate condenser containing an ionized gas. Let C_x be the capacity and Q_x the charge on each plate. In the absence of ions let C be the capacity and Q the charge. Then $VC = Q$ and $VC_x = Q_x$ and so $C_x/C = Q_x/Q$. As the applied potential is made smaller, the region near the plates in which the stronger field exists becomes narrower, and for very small potentials very little error is introduced by assuming that the field intensity half-way between the

¹⁸ John Zeleny, *Phil. Mag.*, **46**, p. 120 (1898).

¹⁹ "Conduction of Electricity through Gases," p. 64.

²⁰ *Terrestrial Magnetism*, **18**, p. 163 (1913).

²¹ 2.7 assuming only recombination of an^2 type. If α is taken as 50×10^{-6} , the maximum ratio becomes 1.14.

plates is the same, whether or not ions are present. Consequently, if X_c is the field at the centre

$$X_c = 4\pi \frac{Q}{\text{Area}}$$

also

$$X_p = 4\pi \frac{Q_x}{\text{Area}}$$

and so

$$\frac{Q_x}{Q} = \frac{X_p}{X_c}.$$

This ratio we have seen may reach the value 2.7, and this then is the maximum ratio of C_x to C . That is, the effective capacity of a condenser of the type indicated may be 2.7 times as great as would be found by the ordinary methods of measurement.

An experimental determination of the ratio of these two capacities was next undertaken. A sensitive electrometer was necessary and on account of the low ionic velocities it was necessary to surround the ionization chamber with a dead air space to prevent air currents which would destroy the desired state of separation of the ions. A condenser was constructed consisting of a box 130 cms. by 100 cms. by 40 cms. in depth, covered at the top and bottom with galvanized iron plates and rendered conducting on the internal walls by conducting black paper. The central plate was 61 cms. by 82 cms. and was surrounded by a guard ring 10 cms. in width. The high potential capacity measured as in the previous work was 43.8 cms.

The method used in measuring the low potential capacity was such as to make unnecessary any correction for ionization current during the experiment. With the central plate connected to the electrometer it and the guard ring were raised to some small known potential and the potentiometer system A (Fig. 1) so adjusted that there was no current across the condenser. The central plate was then disconnected and earthed, the guard ring earthed, the plate then reconnected and both it and the guard ring restored to the original potential. The potential of the plate was raised by changing the potential V_B across the standard condenser C .

The numerical magnitudes involved in a typical determination will be given. The original known potential was 0.0144 volt or

4.80×10^{-5} e.s.u. corresponding to the deflection of 8 cms. on the electrometer scale. The change in V_B required to restore the plate to the above potential after earthing was 0.0198 volt = 6.60×10^{-5} e.s.u. As the capacity C was 68.5 cms., the quantity of electricity required was 4.52×10^{-3} e.s.u., and dividing this by 4.80×10^{-5} gives 94.3 cms. as the low potential capacity, making the ratio of capacities in this case 2.15.

The potentials used were seldom above and sometimes very much below 0.1 volt. This gives an ionic velocity of less than 0.01 cm. per second; thus very slight air currents would be sufficient to prevent the desired conditions from being established. Consequently, consistent results were not obtained, but in a series of observations extending over fourteen days the ratio was always found to be greater than unity and a few values as high as four were obtained. It is felt that this justifies the statement that the effect exists, and that owing to its magnitude it should be taken into consideration when low potentials are used on gas condensers whose plates are some distance apart.

THEOREM.

While carrying out the experimental work indicated previously, it became desirable to know the effect of momentarily earthing the plates of a condenser containing ions, and the following theorem and proof were developed. *Given a closed condenser of any form with any arbitrary distribution of positive and negative ions between its plates. To prove that if the two plates are momentarily earthed and the ions then allowed perfect freedom, in the final state the plates will be at zero potential.*

In the final state there are no charges in the region between the conductors, because if there were, there would be a flux across a surface enclosing them proportional to the enclosed charge. The charges would consequently leave the region.

At the initial instant the conductors take such charges as are necessary to give them zero potential. Consequently in the field which exists due to charges between the plates, there must be at least one surface where the field reverses direction, *i.e.*, becomes zero. By Gauss' theorem the total charge inside this surface is zero. Therefore the volume charge on either side of the surface is equal and opposite to the charge on the neighboring conductor. No charges cross the surface and in the final state no charges

remain in the volume. Consequently these charges neutralize each other, leaving no charges anywhere, and so the conductors are at zero potential.

SUMMARY.

The various methods of determining the coefficient of recombination are briefly indicated, and the general results previously obtained are given.

The coefficient of recombination of ions in air was determined for ions produced by "natural" ionization as opposed to the strong "artificial" ionization usually used in laboratory experiments.

McClung's method, used for some of the observations, was replaced by a new method which requires the measurement of the growth with time of the number of ions per c.c. The diffusion correction is based upon a solution obtained for the equation

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \beta n + q.$$

Results of the present investigation substantiate Von Schweidler's conclusion that for natural ionization in atmospheric air it is more appropriate to determine a recombination coefficient β , depending upon the first power of the number of ions, than to determine an α depending upon the square of this number. The present work also extends this conclusion to the case of confined air subject to various intensities of ionization by α and β rays up to about 400 ions per c.c. per second, and various degrees of purity of the air. It applies also to the case where precautions were taken to remove moisture and dust particles. The value of β was found to be quite constant, averaging about 6×10^{-3} when the ionization intensities and dust content were low. These results show that a recombination depending upon the first power of the number of ions cannot be explained by the presence of dust and moisture. A suggested explanation is that it is due to a non-uniform distribution of ions.

The non-uniform distribution of ions resulting from natural ionization is discussed, and results of a few experiments on columnar ionization given.

A computation based upon the dynamical theory of gases shows that only a comparatively small number of dust particles would be necessary to account for the β term if it were permis-

sible to assume it as due to this cause. The large currents and low values of n , obtained by introducing artificial rain, smoke and steam into the ionization chamber, are explained as due to the production of large slowly moving ions.

Theoretical considerations supported by experimental results show that for low potentials the capacity of an air condenser having the plates some distance (20 cms.) apart, may be increased by the factor 2.7, by natural ionization.

A proof is given for a theorem which states that if the plates of a closed condenser are momentarily earthed, they will in the final state be at zero potential, no matter what the original distribution of ions may be.

In conclusion the writer wishes to express his indebtedness to Professor W. F. G. Swann for suggesting this problem and for his advice and assistance during the progress of the work, and also to Professor J. T. Tate for his assistance and encouragement.

A New Measurement of the Pressure of Radiation. W. GERLACH and ALICE GOLSEN. (*Z. f. Phys.*, vol. 15, No. 1.)—Let it be remembered that Bartolini predicted the existence of a pressure exerted by radiation upon a surface on which it impinges, that Peter Lebedew demonstrated its existence and that Nichols and Hull, at Dartmouth College, measured it with great care. The present investigators set out to make an independent measurement at pressures of surrounding gas so low that nothing akin to radiometer action could complicate the results. A sheet of thin platinum foil was suspended so as to hang to one side of a quartz thread. A beam of light struck the foil and made it turn around the thread as an axis. First a study of the deflections produced by the beam at different gas pressures had to be made. Strangely enough, for the pressure interval from 1 mm. to 2×10^{-4} mm. the foil moved toward the light instead of away from it. As the pressure is reduced the foil shows a push which reaches a maximum at 10^{-5} mm. Further reduction causes a slight lessening of radiation pressure as indicated by angular deflection. Finally the force exerted by the beam became independent of the gas pressure, and there was almost no damping of the oscillations.

These results are given:

1. In a vacuum of from 10^{-6} to 10^{-7} mm. of mercury a constant residual reflection is found, which is interpreted to be due to nothing but the pressure of the incident radiation.
2. This deflection is proportional to the incident energy and is independent of the wave-length of the radiation.
3. The pressure of radiation calculated from the residual deflection agrees within 2 per cent. of the theoretical value.

G. F. S.

THE SHORT-WAVE RADIATION FROM TUNGSTEN FILAMENTS.*

BY

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I. INTRODUCTION.

RADIATION of short wave-lengths is becoming more important each year as studies and applications of radiations increase in extent and number. At the present time the spectral regions of most practical importance are those whose spectral limits are established by the transmission of the atmosphere, of glasses and of quartz. The limit of the spectrum of solar radiation¹ is determined by the contents of the upper atmosphere, apparently, chiefly by ozone. The practical limit is about $295\text{ m}\mu$, although it is not difficult to record $292\text{ m}\mu$ photographically. By means of a quartz spectrograph the last indication of photographic action is found to be at about $290\text{ m}\mu$. The photoelectric cell has recorded solar radiation as short as $280\text{ m}\mu$ in wave-length.

Some glasses transmit approximately as far as the short-wave spectral limit of solar radiation, but the transmission limit is shortened in general as the refractive index of the glass increases. For example, a glass of refractive index of 1.51 transmitted to $295\text{ m}\mu$; a light flint of refractive index of 1.57 transmitted to $305\text{ m}\mu$; and a very dense flint glass of refractive index of 1.69 transmitted only to $335\text{ m}\mu$. However, content also determines the limit of transparency. Owing to the fact that some glasses of low refractive index transmit energy of wave-lengths as short as $295\text{ m}\mu$, a continuous-spectrum source confined in such a glass supplies radiation similar to solar radiation in spectral extent, though not necessarily in spectral distribution of energy.

The limit of transparency of quartz varies somewhat, depending upon the specimen; furthermore, natural quartz crystals are generally transparent further into the ultra-violet than fused quartz. The latter is transparent to $185\text{ m}\mu$, although a practical limit may be considered to be at about $200\text{ m}\mu$.

* Communicated by the Director of the Laboratory.

For convenience the term "near ultra-violet" is given to the region between $300\text{ m}\mu$ and $400\text{ m}\mu$ and the term "middle ultra-violet" to that between $200\text{ m}\mu$ and $300\text{ m}\mu$. The "extreme" region of wave-lengths shorter than $200\text{ m}\mu$ includes the radiations readily absorbed by air and most other media, and also includes gamma rays and X-radiation. The extreme region is of great scientific interest, but is of comparatively little practical interest at the present time.

A great many materials, including solids, liquids, and some gases of appreciable thickness, are transparent only to the near ultra-violet. Among these are mica, "celluloid," diamond, Canada balsam, ether, glycerin, acetone, turpentine, xylene, and many ordinary glasses. Fewer media are transparent to the middle ultra-violet. Among these are rock-salt, fluorite, alum, gypsum, sugar, calcspar, water, ethyl alcohol, glacial acetic acid, liquid ammonia, and fused and crystalline quartz. Of course, the limit of transparency depends upon thickness as well as upon the medium itself so that the foregoing statements are subject to qualifications.¹

However, it is evident that, from a practical standpoint, the spectral transmission limits of glasses and of many other materials make the near ultra-violet of interest. Likewise, the transparency of quartz for the middle region (as well as for the near ultra-violet and visible regions) makes this middle region also of practical interest.

It has been fairly well established that it is the ultra-violet radiation of wave-length shorter than $305\text{ m}\mu$ that is quite injurious to living cells.² Fortunately the cornea of the eye is opaque to radiations shorter than about $295\text{ m}\mu$, thereby protecting the eye-media from the more dangerous rays. The lens is opaque to radiations shorter than $350\text{ m}\mu$ in wave-length, therefore, it may be safely stated that the retina does not receive appreciable amounts of energy of wave-lengths shorter than $350\text{ m}\mu$.

The point in the spectrum at which germicidal action begins has not been established with certainty. Doubtless it varies with the kind of living organism, but in general it is near $300\text{ m}\mu$. Certainly it is within the limit of the solar spectrum, because it is well known that solar radiation is germicidal. Bovie³ found that radiation of wave-lengths shorter than $292.5\text{ m}\mu$ killed bacteria and spores of various fungi in ten minutes, but radiation of $295\text{ m}\mu$

did not kill for two hours. Browning and Russ⁴ found $296\text{ m}\mu$ to be the long-wave limit of germicidal action. Obviously time and intensity are important factors and in the case of solar radiation we have long periods of exposure and intensities of certain radiations not often equalled by artificial means.

It is obvious that another region of importance is that between the vicinity of the spectral limit of solar radiation and of transmission of glasses which probably includes the long-wave limit of general germicidal action. In other words, the region between $290\text{ m}\mu$ and $310\text{ m}\mu$ is of special interest.

One of the rapidly growing fields of application of ultra-violet and visible radiations is that of therapeutics. Unfortunately many of these applications are made without an accurate record of spectral limits and of spectral distributions of energy. Furthermore, many of the data are conflicting; however, the therapeutic values of these radiations have been established.⁵

The increasing number of photochemical reactions and the increasing use of photographic processes add to the interest in short-wave radiation.

The foregoing brief glimpse indicates why it is of interest to study any practical radiant which supplies ultra-violet radiation. Some studies have been devoted to the short-wave region of the radiation from the tungsten filament, but certain desirable data as to the relation of temperature to such factors as spectral limit and photographic action have not been available. Furthermore, it appeared desirable to extend the study of the limits of spectral transmission of glasses which was made by one of the authors quite a number of years ago in connection with the development of a filament lamp for photographic purposes.⁶ At that time the various glasses were studied and a blue bulb was developed which greatly reduced the visible radiation without appreciably impairing the photographic values of the total radiation for most photographic plates and films. Furthermore, a higher operating temperature was adopted for the filament, which was more consistent with the various economic factors involved. During those investigations the interesting discovery was made that by adding a slight amount of cobalt oxide to a certain glass "mix," the limit of spectral transmission was extended appreciably further into the ultra-violet, that is, to a shorter wave-length. Inasmuch as this spectral limit is close to those wave-lengths where germicidal action and

destruction of living cells begins, this point is of particular interest. Some years later this effect of cobalt oxide was verified.⁷

There are various practical ways of studying the ultra-violet radiation from tungsten filaments, but in the present work photography was chosen because photographic value was one of the aims of the investigations. In the spectral work, quartz spectrographs were used entirely. Special filament-lamps were made with quartz windows at the end of a one-inch tube which extended several inches from the side of the bulb. Temperature measurements were made by means of an approved pyrometric method and the photographic action was studied by approved photometric methods. The work is presented in condensed form under several subheads into which it has been divided for presentation.

II. NOMENCLATURE AND DEFINITIONS.

The nomenclature of photography dealing with the exposure and blackening of photographic emulsions has been found by the authors to be meagre and inadequate. For this reason they have introduced certain new terms.¹⁶ The definitions of these and some definitions adopted by the Illuminating Engineering Society are presented in paragraphs which follow.

A *radiator* is a body or object emitting radiant energy.

Intensity of radiant flux or *flux density* is the quantity of energy which traverses, in the unit of time, a unit surface normal to the direction of propagation. It may be expressed in ergs per square centimetre per second.

The *international candle* is the unit of luminous intensity, such as has resulted from international agreement between the three national standardizing laboratories of France, Great Britain and the United States in 1909.

A *lumen* is the unit of luminous flux. It is equal to the flux through a unit solid angle (steradian) from a uniform source of one international candle.

A *metre-candle* (or lux) is the unit of illumination (visual) as used in this paper. It is equal to one lumen per square metre, or it is the direct illumination on a surface which is everywhere one metre distant from a point source of one international candle.

Exposure is the time integral of intensity of radiant flux.

In this paper exposure is expressed in three ways, as follows:

(a) In ergs per square centimetre.

(b) In metre-candle-seconds (luminous efficiency being known).

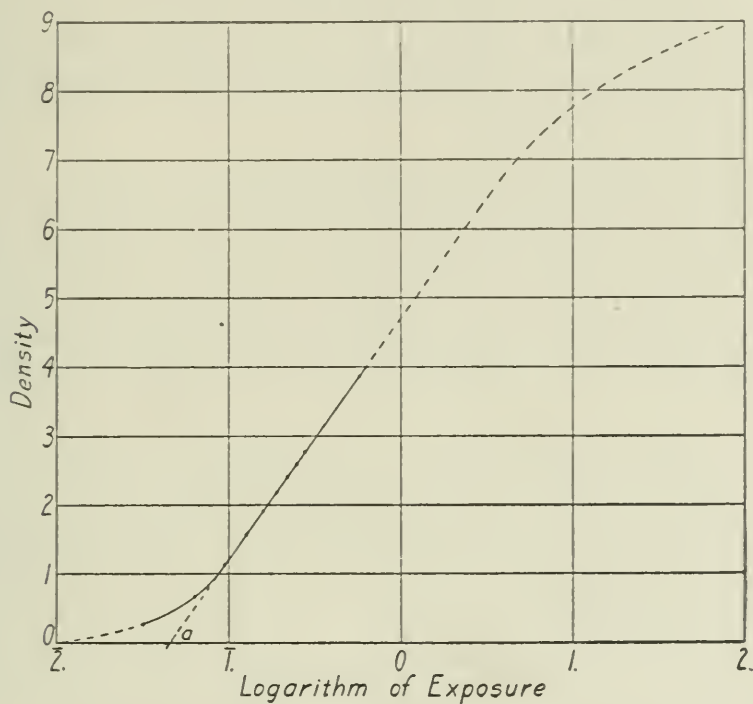
(c) In seconds (intensity of radiant flux being assumed known or constant).

Optical density (D) is defined as $\log_e \frac{1}{T}$, where T is the transmission-factor, measured visually, for energy from a diffuse radiator.

$$D = \log_e \frac{1}{T} = -\log_e T, \text{ or } T = \frac{1}{e^D}$$

where e is the base of the natural logarithms. The transmission-

FIG. 1.



Typical exposure-density curve of a photographic emulsion.

factor is customarily determined relatively to that of an unexposed adjacent portion of the plate, usually called a fog-strip.

Exposure-density Curves.—If different portions of a photographic emulsion are exposed to radiant energy of constant intensity for varying lengths of time, and the resultant densities of these portions are plotted as ordinates and logarithms of exposures as abscissæ, the result is an S-shaped curve having a straight-line portion (Fig. 1). The exposure corresponding to the point of intersection (a) of the tangent to the straight-line portion with

the exposure axis is usually designated as the *inertia* of the emulsion for the particular radiations used. This curve is called an *exposure-density curve*.

Sensitivity (S_λ) of a photographic emulsion to monochromatic radiations of wave-length λ is defined, for the purposes of this paper, as the reciprocal of the inertia in ergs E_λ incident upon one square centimetre of emulsion. Hence sensitivity for wave-length λ is

$$S_\lambda = \frac{1}{\text{Inertia in ergs of wave-length } \lambda} = \frac{1}{E_\lambda}.$$

The *spectral-sensitivity curve* of an emulsion is a curve showing the sensitivity S_λ for each wave-length throughout the spectrum.

The sensitivity of an emulsion varies with the wave-length of the incident radiations. The choice of a numerical value of sensitivity to be assigned to any particular emulsion should be governed by the following desiderata:

- (a) It should be definite and practicable.
- (b) It should be easy to determine and to verify.
- (c) It should indicate approximately the relative speeds of emulsions for practical photography.
- (d) It should be simply related to the maximum sensitivity of the emulsion for monochromatic or nearly monochromatic radiations.
- (e) It should correspond to the value at a wave-length or spectral region in which all commercial emulsions are sensitive.
- (f) The spectral region with which it is associated should be such that sufficient energy for practical tests is readily obtainable from ordinary light-sources.

Possible ways of meeting most of these desiderata would be the adoption of a numerical value of sensitivity defined in some one of the following ways:

- (1) The maximum sensitivity in the violet region of the visible spectrum.
- (2) The sensitivity for some standard wave-length, *e.g.*, 436 m μ of the mercury spectrum.
- (3) The average sensitivity over the selected spectral region from 350 to 450 m μ , in which region the sensitivity of many emulsions is fairly uniform and practically the maximum.
- (4) The average spectral sensitivity of the emulsion over its most effective region.

(5) The average sensitivity to solar radiation at noon, or to some standard heterogeneous source.

As a practical value of the *sensitivity* S of an emulsion which more nearly satisfies the majority of the above desiderata, we adopt for use in this paper the average sensitivity of the emulsion for a narrow spectral region having its average value at about the wave-length of the mercury line $436\text{ m}\mu$.

Therefore the *sensitivity* S of an emulsion is defined as the reciprocal of the inertia in ergs, E , incident upon one square centimetre of the emulsion of practically monochromatic radiation of wave-length $436\text{ m}\mu$, or

$$\text{Sensitivity, } S = \frac{1}{\text{Inertia in ergs of wave-lengths about } 436\text{ m}\mu} = \frac{1}{E}$$

Actinicity, A , of any radiation is defined as the reciprocal of the inertia in ergs, E_r , incident per square centimetre of the emulsion, or

$$\text{Actinicity, } A = \frac{1}{\text{Inertia in ergs of this radiation}} = \frac{1}{E_r}$$

Photographic efficiency, ρ , of any radiation upon an emulsion is defined for the purposes of this paper as the ratio of the inertia in ergs, E , of the standard radiation of practically $436\text{ m}\mu$ in wave-length to the inertia in ergs, E_r , of this particular radiation, or

$$\text{Photographic efficiency, } \rho, = \frac{E}{E_r} = \frac{A}{S} = \frac{\text{Actinicity}}{\text{Sensitivity}}$$

If a photographic emulsion is exposed to radiant energy from an incandescent radiator at various temperatures, less time is required for equal blackening of the emulsion at high than at low temperatures of the radiator. This difference is the result of differences in intensity and actinicity of the radiant energy. Since the effectiveness of the radiant energy in blackening the emulsion is proportional to the reciprocal of the inertia in seconds, *photographic effectiveness* of any radiation of flux density J is defined as the reciprocal of the inertia in seconds for an emulsion of sensitivity S , or

$$\begin{aligned} \text{Photographic effectiveness, } Q &= \frac{1}{\text{Inertia in seconds}} = \frac{1}{t} \\ &= \frac{\text{Flux density in ergs per second}}{E_r} \\ &= \text{Flux density} \times \text{efficiency} \times \text{sensitivity} \end{aligned}$$

As may be seen by reference to Fig. 13, the sensitivity curves of a photographic emulsion and a normal eye vary greatly, being quite different in shape and affected by radiations of more or less different wave-lengths. Therefore it is evident that exposures given in terms of visual sensations for radiations of different spectral distributions of flux density give no *direct* measure of intensity of energy incident upon the emulsion. For this reason exposures and inertias given in metre-candle-seconds are faulty measures of energy, and all factors when so expressed will be preceded by the word *pseudo*, indicating false; thus,

*Pseudo-actinic*ity of any radiation is defined as the reciprocal of the inertia, in metre-candle-seconds, of radiation incident upon the emulsion of sensitivity S , or

$$\text{Pseudo-actinicity, } A_p = \frac{1}{\text{Inertia in metre-candle-seconds}}$$

If a radiator of area A , of a brightness of B candles per square centimetre, radiates W watts from each square centimetre of radiator at a luminous efficiency of L lumens per watt, then an emulsion placed d centimetres from the radiator and normal to the direction of propagation will in t seconds receive E_r ergs per square centimetre, or $E_r = \frac{AWt}{4\pi d^2} \times 10^7$ ergs per square centimetre.

Now since total lumens = πBA , the lumens per watt, $L = \frac{\pi BA}{AW} = \frac{\pi B}{W}$. Therefore, substituting for W from this equation, we have

$$\begin{aligned} E_r &= \frac{A \pi B 10^7 t}{4 \pi d^2 L} = \frac{A \pi B}{4 \pi \left(\frac{d}{100}\right)^2 t} \frac{10^7}{(100)^2} L \\ &= (\text{metre-candle-seconds}) \times \frac{10^3}{L} \text{ in ergs per square centimetre} \end{aligned}$$

Hence, exposures expressed in metre-candle-seconds may be converted into exposures expressed in ergs per square centimetre by multiplying by the factor $\frac{10^3}{L}$. This is the energy which would reach the emulsion if the interposed medium reduced the total energy of all wave-lengths in the same proportion as it reduces the energy which produces visual sensation.

Temperatures in this paper are expressed in degrees Kelvin, °K.

III. ACTINICITIES OF RADIATION FROM TUNGSTEN AT VARIOUS TEMPERATURES THROUGH VARIOUS MEDIA AS MEASURED BY FOUR REPRESENTATIVE PHOTOGRAPHIC EMULSIONS.

The relative photographic efficiencies of various radiants have previously been studied by the authors and others.⁸ This investigation was conducted for two primary purposes: (1) To determine the change of actinicity of the radiation from incandescent tungsten with temperature of the tungsten; (2) to determine the decrease of actinicity of the radiation after traversing specimens of glass (chiefly those used in tungsten-filament lamp-bulbs). The development of the plates was standardized and maintained so throughout all the investigations. Its details are not important from the standpoint of the aims of the investigation.

Apparatus and Methods.—The photographic apparatus employed in this investigation consisted of the following parts arranged along a photometer bar in the order mentioned below:

(1) A specially constructed 1000-watt, 30-ampere, U-shaped tungsten-filament in a gas-filled "hard" glass bulb fitted with a quartz window; (2) a quartz lens for collecting and focusing the light; (3) an iris diaphragm and a shutter for use in controlling the length of exposures; (4) a rough-ground fused-quartz plate on which the image of a portion of the filament was focused; (5) several black-velvet screens which effectually intercepted and absorbed all extraneous light; (6) a rotating multi-sectored disc with ten different angular openings which gave eleven different exposures per strip upon the photographic plate; (7) a slit of $\frac{3}{8}$ -inch width lengthwise of the photographic plate; (8) a plate-holder which could be adjusted to any position with reference to the slit.

Six exposure strips made under varying conditions were obtained on each plate. Approximately identical strips were obtained by suitably varying the exposure when the test conditions were varied. The reciprocity law has been assumed, *i.e.*, that under any particular conditions, the plate density produced is a function of the product of radiant flux density and exposure time, and is independent of the relative values of these factors. This assumption is not rigidly correct, but is approximately so under the conditions of the tests.

The true absolute temperatures of the lamp filament were measured by optical pyrometer methods by Dr. W. E. Forsythe

of the Laboratory of Pure Science for various temperatures up to about 3400° K. Standardized potentiometers were used for measuring the current through the lamp filament, and the intensity of illumination at the plate was measured by a photometer. The lamp, diffuser and other apparatus were rigidly connected together upon a carriage which could be moved to any desired distance from the photographic plate, and by employing the law of inverse squares any intensity of illumination upon the photographic plate could be obtained and calculated with precision.

The apparatus for measuring the densities of the photographic negatives consisted of: (1) An integrating sphere illuminated within to a constant brightness; (2) a movable constant-intensity comparison lamp which illuminated a milk-glass diffusing surface; (3) a bi-prism and two 45° prisms which reflected the two beams at right angles. The light from one of these beams traversed the exposed portion of the negative and the other beam traversed the "fog-strip" of the negative. The apparent brightnesses of these two surfaces were brought to an equality by moving the comparison lamp, and, when necessary, by using a rotating sector disc in the path of one or the other of the beams.

Types of Emulsions.—The photographic emulsions employed were standard $4'' \times 5''$ dry plates manufactured by the Eastman Kodak Company, and were of the following types:

- (a) Seed's No. 26, of emulsion No. 5431.
- (b) Seed's No. 23, of emulsion No. 4880.
- (c) Standard orthonon, extremely rapid, of emulsion No. 4338.
- (d) Wratten and Wainwright panchromatic, sensitive to red light, of emulsions Nos. 3310 and 3404.

Glasses Tested.—The glass and other transmission media employed were as follows:

- (1) A specimen of type No. 5 soft glass, about 0.91 mm. thick. This is a soda-lead glass with 20 per cent. lead oxide.
- (2) A specimen of Pitney lime glass about 0.95 mm. thick. This is a soda-lime glass with 17 per cent. sodium oxide, 10 per cent. calcium and magnesium oxides, and balance of silica.
- (3) A specimen of G 702 P hard glass about 0.96 mm. thick. This is a boro-silicate glass of the "pyrex" type.
- (4) A specimen of bulb of the Mazda C-2 daylight lamp,

about 0.96 mm. thick. This is the same as (1), type No. 5, but contains certain coloring ingredients.

(5) A specimen of bulb of the Mazda C-3 photographic lamp, about 0.95 mm. thick. This is the same as (1), type No. 5, but contains certain coloring ingredients.

(6) A specimen of quartz about 1.5 mm. thick.

(7) A specimen of quartz about 1.5 mm. thick with a sufficiently thick deposit of tungsten metal to reduce its transmission in the visible to about 9.8 per cent.

Results.—Exposure-density curves were made for the five types of bulb-glass, with each type of photographic plate and over wide variations in temperature of filament; and from them was determined the pseudo-actinicities corresponding to each temperature.

Approximately 4 per cent. of the light incident upon a specimen of clear glass in air is reflected from each surface, but, with a lamp-bulb made of this same kind of glass, practically no light is finally lost on account of reflections. In order to reduce all data to a comparable basis an allowance of 8 per cent. for reflections from the specimens has been made in all cases, since this 8 per cent. actually was lost under the test conditions. Hence, neglecting experimental errors, observed differences of pseudo-actinicities at any temperature are due only to differences in amount and character of the absorption of the incident radiations by the interposed media.

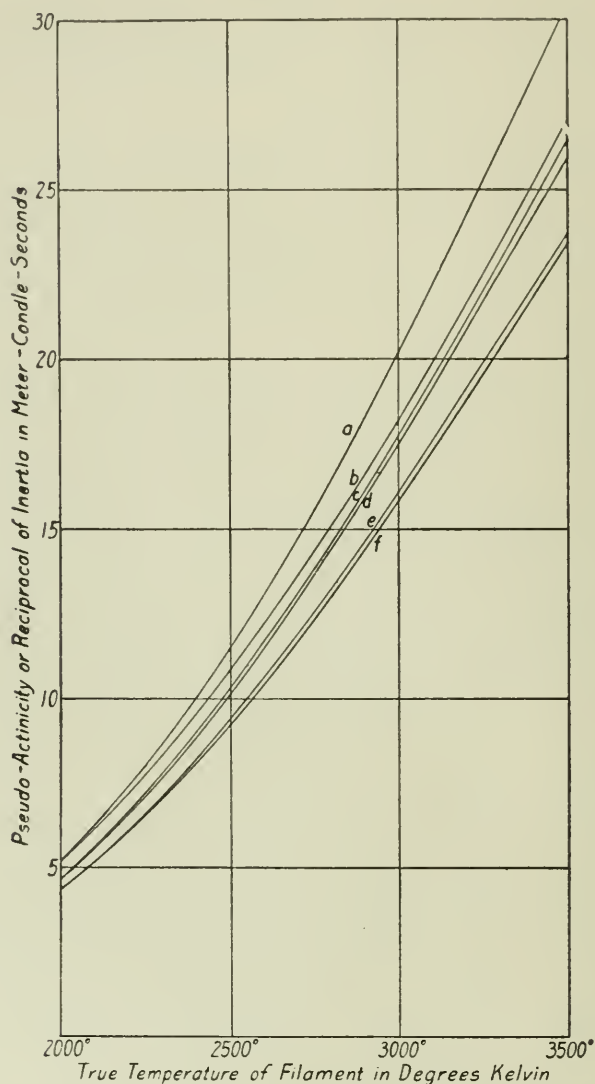
From pseudo-actinicities-temperature curves obtained experimentally, values were scaled off corresponding to temperatures of 2000, 2200, 2400, 2600, 2800, 3000, 3200 and 3400° K. for each type of glass and each type of photographic plate, and these have been tabulated in Table I. The comparative data for a Seed's 26 plate are shown in Fig. 2. Pseudo-actinicities for the same emulsion based on metre-candles measured at the plate with glasses interposed are shown in Fig. 16.

A study of the effect of blackening or deposit on lamp-bulbs during the operation of tungsten lamps was made to determine whether this deposit is selective in transmission. It was found to be only slightly selective, that is, the decrease due to a normal deposit on the inside of lamp-bulbs was only slightly greater for actinic radiations than for luminous radiations. However, a very

dense deposit which reduced the luminous radiations to 9.8 per cent. reduced the actinic radiations to approximately 5.8 per cent.

Inherent in photography, measurements of illumination, temperatures and optical densities, there are numerous variables

FIG. 2.



Pseudo-actinic ($1 \div \text{inertia in metre-candle-seconds}$) curves for radiant flux from tungsten as effective on Seed's 26 plates, illumination being measured at the plate without the glass interposed, and deducting 8 per cent. for reflections when the glasses are interposed. (a) Quartz; (b) soda-lead; (c) soda-lime; (d) boro-silicate; (e) C-2 daylight; (f) C-3 photographic.

and experimental errors which affect the determinations. Since considerable care has been exercised in controlling these variables, it is believed that the results are substantially correct, though containing a few minor inconsistencies.

TABLE I.

Table showing values of pseudo-actinicities of radiations from incandescent tungsten at various temperatures through various media upon four types of emulsions, the metre-candles upon the emulsions being measured without the glass specimens interposed and deducting 8 per cent. for reflections by the interposed glass. The pseudo-actinicities are the reciprocals of the inertias which are expressed in metre-candle-seconds.

Interposed medium.	Pseudo-actinicities or reciprocal of inertias in metre-candle-seconds for temperatures indicated.							
	2000° K.	2200	2400	2600	2800	3000	3200	3400° K.
<i>Seed's 26 Plate</i>								
Quartz.....	5.2	7.4	10.0	13.0	16.4	20.1	24.2	28.4
Soda-lead.....	4.7	6.6	9.0	11.7	14.5	17.7	21.1	24.7
Soda-lime.....	5.2	7.2	9.6	12.2	15.1	18.2	21.6	25.2
Boro-silicate.....	4.4	6.0	8.1	10.4	13.0	15.8	18.8	21.9
C-2 daylight (light blue)....	4.7	6.6	8.9	11.5	14.3	17.5	20.8	24.3
C-3 photographic (dark blue)	4.4	6.1	8.2	10.6	13.2	16.1	19.1	22.2
<i>Seed's 23 Plate</i>								
Quartz.....	2.4	3.2	4.2	5.4	6.7	8.1	9.7	11.3
Soda-lead.....	2.2	3.0	4.0	5.1	6.3	7.7	9.1	10.6
Soda-lime.....	2.3	3.1	4.1	5.2	6.5	7.8	9.4	10.9
Boro-silicate.....	2.1	2.9	3.8	4.9	6.1	7.4	8.9	10.4
C-2 daylight (light blue)....	2.0	2.8	3.8	4.9	6.2	7.5	9.0	10.5
C-3 photographic (dark blue)	2.0	2.8	3.9	5.0	6.3	7.7	9.2	10.8
<i>Orthonon Plate</i>								
Quartz.....	6.4	8.4	10.9	13.6	16.5	19.8	23.4	27.3
Soda-lead.....	5.2	7.3	9.8	12.5	15.5	18.7	22.3	26.0
Soda-lime.....	6.2	8.0	10.0	12.4	15.0	17.8	20.8	24.0
Boro-silicate.....	4.7	6.3	8.3	10.5	12.9	15.6	18.5	21.5
C-2 daylight (light blue)....	5.2	7.1	9.3	11.8	14.6	17.6	20.9	24.2
C-3 photographic (dark blue)	4.8	6.6	8.6	10.9	13.5	16.3	19.3	22.5
<i>Panchromatic Plate</i>								
Quartz.....	2.3	3.1	4.1	5.2	6.4	7.7	9.1	10.6
Soda-lead.....	2.1	2.9	3.8	4.9	6.1	7.4	8.9	10.4
Soda-lime.....	2.2	3.0	4.0	5.1	6.3	7.6	8.9	10.4
Boro-silicate.....	2.1	2.7	3.4	4.3	5.2	6.2	7.4	8.6
C-2 daylight (light blue)....	2.2	2.7	3.4	4.2	5.1	6.1	7.2	8.3
C-3 photographic (dark blue)	1.9	2.3	2.8	3.4	4.0	4.8	5.7	6.6

IV. SPECTRAL TRANSMISSION OF THE VARIOUS LAMP-BULB GLASSES.

The glasses studied are described in Part III but the thicknesses differ, being as follows:

Type of Glass.	Thickness.
No. 5 soda-lead	0.84 mm.
Pitney lime	0.80
Hard glass, G702P	1.05
Mazda C-2 daylight bulb	0.47
Mazda C-3 photographic bulb	0.52

Apparatus and Method.—The apparatus consisted of the following: A quartz prism spectrograph; a quartz lens; a diffusely transmitting quartz plate; a quartz tube mercury lamp; a special tungsten lamp with quartz window and a 20-mil. filament in gas; sectored discs; dividing engine; Marten's polarization photometer with 0.5-mm. slit through which the exposed photographic plate was viewed when measuring the densities of the silver deposit.

Three methods were employed in making the determination of spectral transmission:

(1) By the use of the special tungsten lamp continuous spectra were obtained. Exposures for different lengths of time were made with and without the specimens of glass interposed. The photographic plates were measured for density, and exposure-density curves plotted for various wave-lengths throughout the spectrum. From these curves inertias (expressed in time units only) were obtained. The ratio of observed inertias without and with the bulb-glass interposed, for any particular wave-length, gives the transmission of the glass for that wave-length. This method involves a great deal of labor, and is subject to many errors. The results obtained were of value, but not as satisfactory as desired.

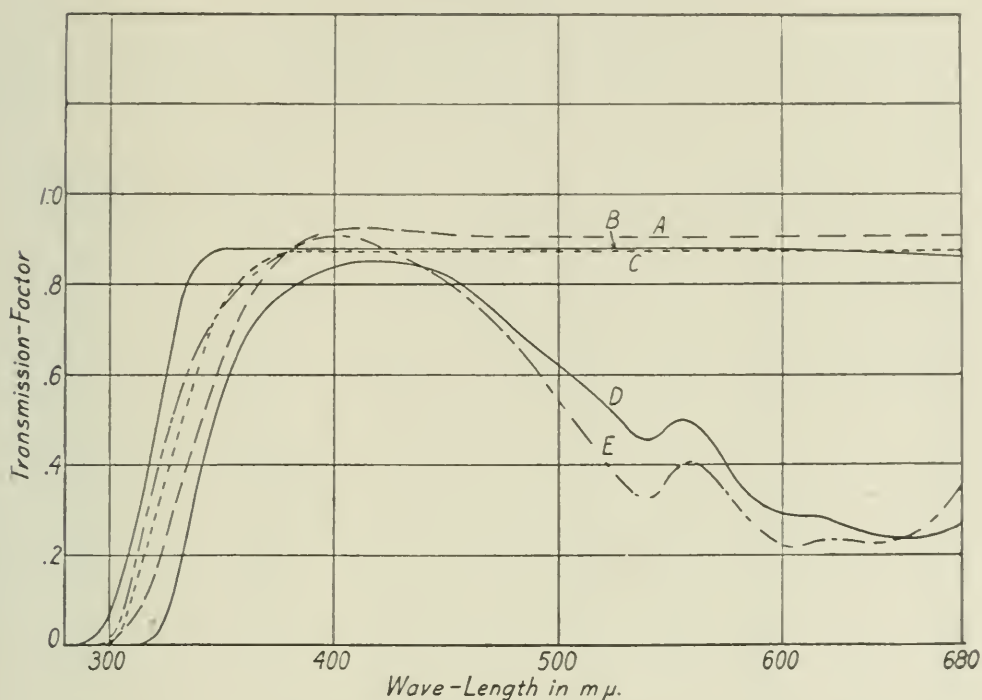
(2) By using a spectrophotometer, with visual observation, transmission factors were obtained for each type of glass for the spectral region from 420 $m\mu$ to 700 $m\mu$. Values obtained by this method for wave-lengths below 460 $m\mu$ were somewhat uncertain, on account of the low illumination in the photometer field, but were quite satisfactory throughout the remainder of the region measured.

(3) This was also a photographic method. Using the quartz spectrograph, adjacent exposures were made on photographic plates. Alternate exposures were made with the bulb-glass interposed between the lamp and the quartz diffuser placed just in front of the spectrograph slit, and the other exposures were made with the bulb-glass removed. By means of the polarization photometer the point in the spectrum at which two adjacent exposed strips were of equal density was determined, and the corresponding wave-length found by reference to the quartz mercury spectrum on the plate. If t' is the exposure in seconds with the bulb-glass interposed, and t'' the exposure without the glass, then the trans-

mission-factor at the point of equal density of silver deposit is $\frac{t''}{t'}$. This method yields satisfactory results for transmissions on the steep part of the transmission curve, but is not sensitive over portions of the curve where the transmission is changing slowly.

In order to make the transmission data for the various glasses comparable, the observed values have been adjusted by the method devised by one of the authors,¹⁴ to give transmissions for glasses

FIG. 3.



Spectral transmission curves for lamp-bulb glasses 0.8 mm. thick: (A) Boro-silicate hard glass; (B) soda-lime; (C) soda-lead; (D) Madza C-2 daylight; (E) Madza C-3 photographic.

of a uniform thickness of 0.8 mm. The adjusted values are given in Fig. 3 and Table II, without any correction for reflection.

SPECTRAL LIMITS OF GLASSES AND LENSES.

Many years ago one of the authors⁷ found that the limit of spectral transmission of a soda-lead glass was extended farther into the ultra-violet when cobalt was added. This is clearly illustrated in Fig. 4, in which each pair of spectra for clear and cobalt glass was obtained by simultaneous exposure, using an iron arc, a quartz mercury arc and a quartz spectrograph. The various pairs were for different exposures.

In Fig. 5 are given spectrograms of some glasses used in this investigation. These spectrograms were obtained by the use of a

quartz spectrograph, with slit about 0.5 mm. wide (so that density measurements could be made) and a quartz mercury lamp.

In Fig. 6 are given spectrograms of glasses like most of those in Fig. 5, but of a uniform thickness of approximately 0.8 mm. In this spectrogram are also included two glasses like the ordinary Mazda C-2 daylight and Mazda C-3 photographic glasses, except that they are made up by the addition of coloring material to the

TABLE II.

Table of transmissions of lamp-bulb glasses for wave-lengths in the visible and near ultra-violet regions for glasses of a uniform thickness of 0.8 millimetre.

Wave-length in $m\mu$.	Spectral transmission of lamp-bulb glasses 0.8 mm. thick.				
	No. 5 soda-lead.	Soda-lime.	Boro-silicate.	Mazda C-2 daylight bulb.	Mazda C-3 photographic bulb.
300 $m\mu$.01	.07	.005	.0	.015
320	.28	.47	.15	.017	.365
340	.62	.845	.49	.375	.665
360	.82	.88	.745	.675	.805
380	.875	.88	.875	.785	.875
400	.875	.88	.92	.84	.91
420	.875	.88	.925	.85	.885
440	.875	.88	.915	.84	.84
460	.875	.88	.905	.79	.77
480	.875	.88	.905	.70	.67
500	.875	.88	.905	.62	.545
520	.875	.88	.905	.535	.41
540	.875	.88	.905	.455	.325
560	.875	.88	.905	.495	.405
580	.875	.88	.905	.36	.305
600	.875	.88	.905	.29	.22
620	.875	.875	.905	.28	.235
640	.875	.87	.905	.245	.225
660	.875	.865	.905	.235	.25
680	.875	.86	.905	.27	.36

soda-lime glass instead of the soda-lead which is ordinarily used. Four spectrograms of commercial photographic lenses are also given. The iron arc was used and quartz mercury arc spectra are shown for comparison.

In Fig. 7 are given spectrograms of a tungsten filament at a temperature of 3000° K., with varying lengths of exposure. An examination of the negative for the 15-minute exposure shows that blackening of the plate extends to about 230 $m\mu$.

The spectrograms shown in Fig. 6 and other similar ones have been scaled to determine the extent of the transmission of ultra-

violet radiations by the various glasses and lenses. The results obtained are given in Table II A.

V. SPECTRAL SENSITIVITIES OF FOUR TYPES OF PHOTOGRAPHIC EMULSIONS.

Spectral sensitivities of the four types of photographic emulsions described in Part III have been determined for various wave-lengths throughout the spectral region between 280 mμ and 580 mμ. A series of exposures was made upon a Seed's 23 emul-

TABLE II A.

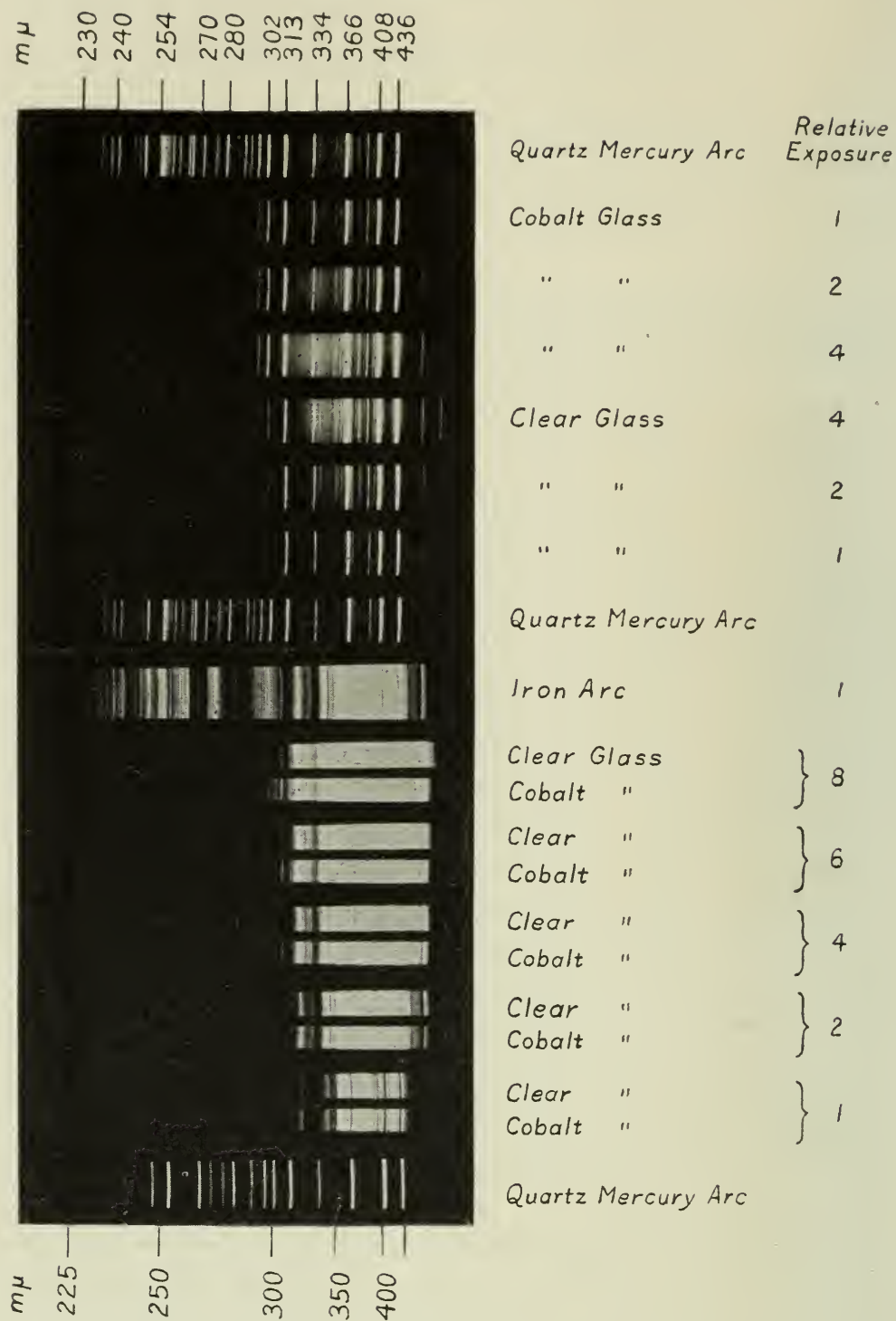
Table showing approximately the shortest wave-lengths of radiation from an iron arc that have traversed various absorbing media and the quartz optical system of a Hilger spectrograph and that are sufficiently strong to make observable lines upon a Seed's 23 emulsion in the exposure times indicated.

Interposed media.	Shortest wave-lengths, in mμ, of radiations producing observable lines.					
	½ min.	1 min.	2 min.	3 min.	4 min.	5 min.
Soda-lead.....	295.4	295.4	295.0	294.2
Soda-lime.....	288.4	284.0	283.2	282.3
Boro-silicate.....	298.4
C-2 soda-lead.....	304.2
C-2 soda-lime.....	302.0
C-3 soda-lead.....	296.0	295.4	295.0	294.2	294.2	294.2
C-3 soda-lime.....	294.2	293.8	292.9	292.9	292.5	291.8
*Cooke lens.....	321.4	321.2	321.2
Zeiss Tessar lens.....	320.0	319.7	319.7
Std. Opt. Co. lens....	339.3	339.3	337.0
B. and L. Protar lens..	330.6	330.6	330.6

*Made by Taylor, Taylor and Hobson.

sion by using a quartz spectrograph to disperse the continuous spectrum of a tungsten radiator maintained at a temperature of 3060° K. From transmission measurements upon this emulsion, exposure-density curves were plotted; and by the method described in Part II the inertias in seconds corresponding to various wave-lengths were obtained. The dispersion of the spectrograph was determined and the intensity of radiant flux for incandescent tungsten at various wave-lengths was computed by use of equation (13) described in Part VI, where T_c , the color temperature of tungsten at 3060° K., is 3140° K. Hence, knowing the relative inertias of this emulsion at various wave-lengths of the continuous spectrum of tungsten at 3060° K., the dispersion of the spectrograph, and the intensity of radiant flux throughout the tungsten spectrum, the relative sensitivities for this emulsion for a uniform

FIG. 4.



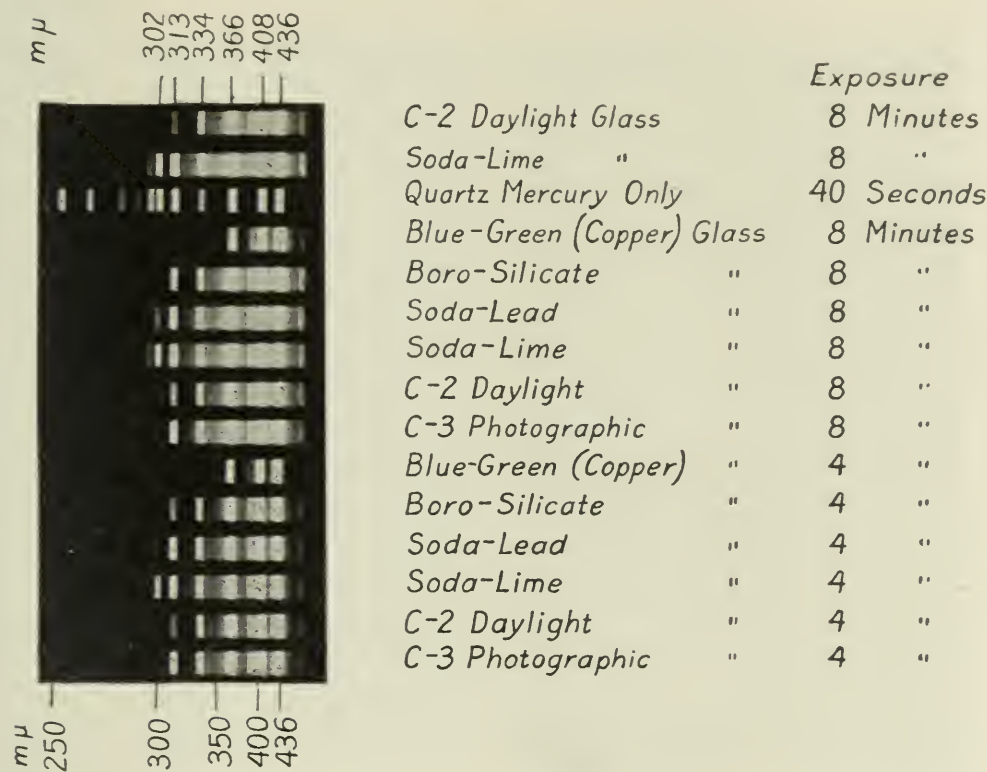
The transmission of clear and cobalt glasses for ultra-violet radiation of bare iron arc and quartz mercury arc.

(From "Ultra-violet Radiation" by M. Luckiesh.)

distribution of radiant flux were computed for various wave-lengths and the results plotted in a curve similar to Fig. 8. In a similar manner the spectral sensitivities for a uniform distribution of radiant flux might have been determined for each of the other emulsions; however, for practical reasons the method employed was as follows:

By using a moderately wide slit on the quartz spectrograph a series of spectrograms of a quartz mercury arc was made upon

FIG. 5.



Spectrograms of radiation from quartz mercury arc through various lamp-bulb glasses.

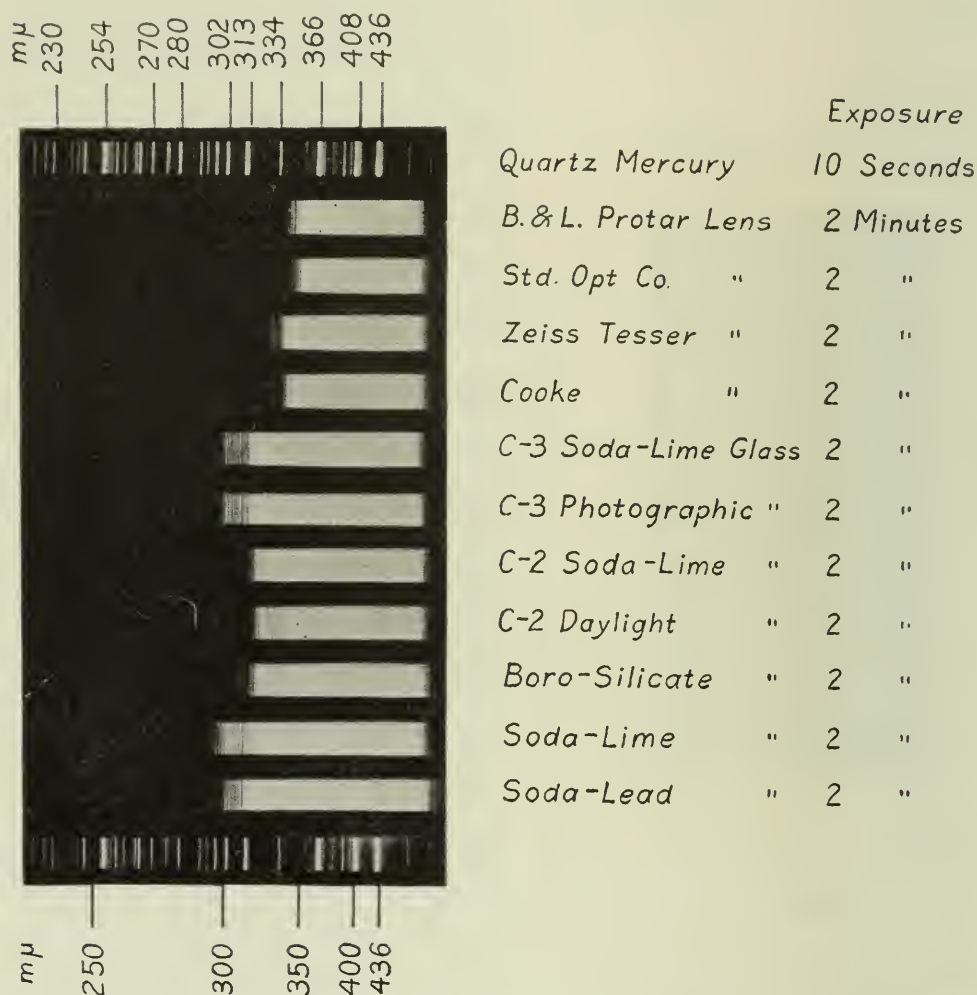
each type of emulsion under identical conditions. From exposure-density curves, plotted for each line of the mercury spectrum, inertias were obtained for each type of emulsion and from them the sensitivity of each type of emulsion was found in terms of the Seed's 23 emulsion. Then to obtain the relative spectral sensitivities of each emulsion, *i.e.*, for a uniform distribution of radiant flux, these relative sensitivities were multiplied by the relative spectral-sensivities of the Seed's 23 emulsion obtained for the continuous spectrum of uniform flux density. The results

for all four types of emulsions were plotted in curves similar to those in Fig. 8.

Relative spectral-sensitivity curves having been obtained for each type of emulsion, it was necessary to find their absolute sensitivities, which was done as follows:

From data in Table I, Part III, the pseudo-actinicities of the

FIG. 6.

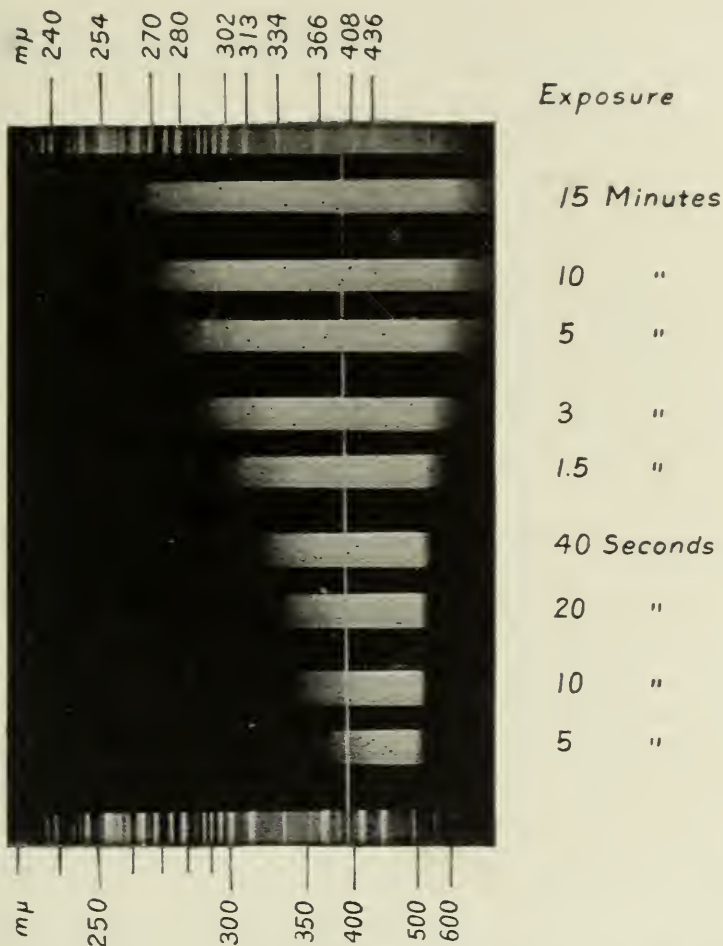


Spectrograms of radiation from bare iron arc through various lamp-bulb glasses, and through four types of photographic lenses.

radiations from tungsten at 3060° K. through quartz is 8.55 for a Seed's 23 emulsion. From Fig. 15, Part VI, the luminous efficiency of this radiation is 23.9 lumens per watt; and therefore the total number of ergs of this radiation per square centimetre of emulsion is 4.9. Assuming the Seed's 23 emulsion to be of practically uniform sensitivity for all wave-lengths between $300\text{ m}\mu$ and

450 $m\mu$ and observing that these short-wave radiations produce 61 per cent. of the total blackening of the emulsion, we have found the total equivalent energy of these short-wave radiations by computing their proportion of the whole by use of equation (13), Part VI. Thus we find the inertia in ergs per square centimetre of radiation of wave-length 436 $m\mu$ for a Seed's 23 emulsion to

FIG. 7.



Spectrograms of radiation from tungsten at 3000°K. through quartz, with various lengths of exposure.

be .075 and the corresponding sensitivity S to be $1/.075$ or 13.3. Similarly the inertia in ergs per square centimetre of a Seed's 26 emulsion for radiation of wave-length of 436 $m\mu$ was computed to be .0312 and the corresponding sensitivity to be $1/.0312$ or 32.

Spectral sensitivity curves for all four types of emulsions are shown in Fig. 8, in which the ordinates are true sensitivities or the reciprocal of inertias in ergs per square centimetre.

(To be concluded.)

Determination of the Ratio of the Two Specific Heats of Carbon Dioxide. BRUNO TORNAU. (*Zeit. f. Physik.*, Dec. 9, 1922.)—In gases with several atoms in each molecule there exists a definite relation between the energy of translation of the molecule and its internal energy, which is permanent as long as a state of equilibrium is maintained. Upon this relation depends further the ratio of the specific heat at constant pressure to that at constant volume. The assumption has been tacitly made that the same ratio between the energies is established no matter how short a time be allowed for the redistribution of the energies concerned. The author sets himself the problem of finding whether he can discover any variation of the ratio in consequence of the shortness of time allowed, and he gets his solution by studying the velocity of sound, which is known to depend on the ratio of the two specific heats, as dependent on the number of vibrations per second of the tuning fork source. Carbon dioxide was used because it is an imperfect gas and might be expected to manifest a departure from uniformity. He found that the velocity of sound was the same within the limits of experimental error with waves originating from forks of 256, 512 and 1024 double vibrations per second, and that the ratio of the specific heats and consequently the ratio of the two quantities of energy were likewise independent of the changes in the pressure of the gas traversed by the sound wave. The ratio of the specific heats came out equal to 1.3165. G. F. S.

On the Longitudinal Elasticity and Poisson's Ratio of India Rubber. G. B. DEODHAR ALLAHABAD. (*Phil. Mag.*, March, 1923.)—Though we are all fairly familiar with some of the elastic properties of this substance it is none the less interesting to have our crude observations confirmed by careful experiments. For example, a piece of old rubber cord was 19.25 cm. long when a weight of 520 grams stretched it and its cross-section had then an area of .3771 sq. cm. For a weight of 5020 grams the length became 49.87 cm. and the cross-section .1536 sq. cm.

"A close scrutiny of the length-tension curve shows that up to a point where the stretched length is about $5/4$ times the original length, a linear relation between length and tension holds good. Then, after that, there is a bend till the stretched length attains about twice the original value; after that, up to the breaking point, a linear relation holds good again. . . . The second linear relation is more conspicuous than the first one as its range is larger." Young's Modulus is far from being a constant, increasing with added weights until it becomes as much as four times its original value. For the same experimental range Poisson's ratio sinks from .87 to .38. There is so much variation in the elastic properties of india rubber that it is quite remarkable to find that the ratio of the square of the length to Young's Modulus is nearly a constant over the two ranges where the linear relations above mentioned hold. G. F. S.

THE COLORING AND THERMOPHOSPHORESCENCE PRODUCED IN TRANSPARENT MINERALS AND GEMS BY RADIUM RADIATION.*

BY

S. C. LIND, Ph.D., and D. C. BARDWELL.

IN an earlier paper¹ one of us reported some observations on the coloring, decolorization and thermophosphorescent effects resulting from the radiation of glass by radium rays. Similar experiments, extended to transparent minerals and gems, are described in the present paper.

The following terminology has been adopted:

	No Radiative Stimulation.	Radiative Stimulation	
		Without After-effect.	Causing After-effect.
No Thermal Stimulation	<i>Luminescence</i>	<i>Fluorescence</i>	<i>Phosphorescence</i>
With Thermal Stimulation	<i>Thermolumines- cence</i>	<i>Thermofluores- cence</i>	<i>Thermophospho- rescence</i>

By thermal stimulation in general is meant that produced by raising the temperature above the normal, but this is not to be understood as precluding the possibility that a phosphorescent effect at ordinary temperature may vanish at a lower one, showing it to have been really thermal in nature. By radiative stimulation is meant that by any radiation (including corpuscular) except that form included under heat radiation. Under this usage the term *thermoluminescence*, previously used, becomes thermophosphorescence. A study of luminescence and thermoluminescence (new definition) is not included in the present paper.

* Communicated by Dr. R. B. Moore, Chief Chemist, U. S. Bureau of Mines, and Associate Editor of this JOURNAL. Communication from the Rare and Precious Metals Experiment Station, U. S. Bureau of Mines, in Coöperation with the University of Nevada. Published by permission of the Director, U. S. Bureau of Mines.

¹ S. C. Lind, *Jour. Phys. Chem.*, **24**, 437-43 (1920).

This subject has already been studied by various investigators.² The results recorded here are in the main confirmatory of previous observations, though complete agreement is not to be expected owing to the variations encountered from specimen to specimen of the same material. It therefore seems desirable to report all the results, although many of them duplicate those of previous investigations, in order to be able to consider them together with the other effects described, many of which are new. An additional reason for the joint consideration of decolorization and thermophosphorescence is found in the possible theoretical connection between the two which will be more fully discussed later in the paper.

The diamond is so unique in its behavior under radium radiation that it will be separately considered in a subsequent communication. In all cases, except the diamond, coloring is produced by the penetrating (beta and gamma) radiation received through a glass wall of ordinary thickness ($\frac{1}{2}$ to 1 mm.). The diamond, however, did not change color under penetrating radiation, even though prolonged and intense, but responded in every case to direct alpha radiation, either from emanation or by direct exposure to radium salts.

Fluorescent effects are caused in some minerals (kunzite, "active" calcite, willemite, etc.) both by alpha and by penetrating radiation, but in most minerals alpha radiation is the only one producing phosphorescence, while many other minerals do not fluoresce even under its stimulus.

In the following, where radiation is reported in terms of *mgs. of Ra*, we refer to the penetrating radiation from high-grade salt (chloride or bromide), 70 to 100 per cent. pure, placed immediately in contact with the mineral and separated only by the glass wall of the container. Where *emanation* is specified, the mineral has been sealed in a glass tube containing radium emanation furnishing alpha, beta and gamma rays. As in the case of glass, the same color is produced in a given specimen (except diamond),

² A. Miethe, *Ann. d. Phys.*, **19**, 633 (1906). C. Doelter, "Das Radium und die Farben," Steinkopf, Dresden, 1910, also "Die Farben der Mineralien, Insbesondere der Edelsteine," Vieweg und Sohn, Braunschweig, 1915. E. Newberry and H. Lupton, *Memoirs and Proc. Manchester Lit. and Phil. Soc.*, **62**, No. 10 (1918). St. Meyer and K. Przibram, *Sitzb. Akad. Wiss. Wien*, **123**, IIa, 653-63 (1914). K. Przibram, *ibid.*, **130**, IIa, 265-70 (1921). St. Meyer and E. v. Schweidler, "Radioaktivität," Teubner, Leipzig-Berlin (1916), pp. 191-7; Lit. refs., p. 198. A. Dauvillier, *Comp. Rend.*, **171**, pp. 627-9 (1920).

either by emanation or by penetrating rays, more rapidly by the former.

Thermophosphorescence was observed visually by placing freshly radiated specimens in an electrically heated muffle, inspecting in the dark with well-rested eye the light emitted upon gradually raising the temperature. In the case of direct radiation by means of emanation the observations were not made until at least four hours had elapsed after removal of the specimens from the emanation in order to allow the active deposit to decay, thus avoiding any direct fluorescent effects.

The observations for individual minerals were as follows:

Rock salt is readily colored to an amber yellow by 250 mgs. Ra in one to two days. It is easily restored to colorless by heating to 300° C. without thermophosphorescence, or by exposure to direct sunlight for one to two hours. Decolorization by diffused light is much slower. The cycle can be indefinitely repeated from color to colorless, either by heat or light, and back to color by radiation.

Through the kindness of Drs. A. W. Hull and W. P. Davey of the General Electric Company, X-ray diffraction spectrographs by the powder method³ were made both of the colorless and of radium-colored crystals. As will be seen (Fig. 1) the two lattice patterns are identical, showing that no change is produced in the colored specimen which can be detected by the X-ray spectro-



FIG. 1.

³ A. W. Hull, *Phys. Rev.*, **10**, 661 (1917); **17**, 571 (1921); *Proc. Am. Inst. Elec. Engs.*, **38**, 1171 (1919); *J. Am. Chem. Soc.*, **41**, 1168 (1919).

graphic method. The question of the displacement of *electrons* is discussed later in the paper.

Fluorspar.—Different varieties, purple, green, rose, and colorless, are readily colored in one to three days by 250 mgs. Ra to various shades of blue and greenish-blue, which color is easily removed by sunlight or by heat. Thermophosphorescence is striking (next in intensity to kunzite) and like kunzite begins at a low temperature. At 70° C. the light is blue, changing to greenish-blue at 125° and remaining unchanged at 150°. At about 180° the crystals decrepitate and the color produced by radium is discharged. A specimen of rose-colored fluorspar could be colored bluish-green repeatedly under radiation and the rose color repeatedly restored either by heating or by light. On the contrary, the purple variety became white at the decrepitating temperature and could not again be colored by further radiation. These observations appear to support the organic coloring theory for the purple varieties, but not for the rose colored.

Kunzite.—Different specimens of California kunzite behave with remarkable uniformity both as regards coloring and thermophosphorescence. Under radiation from 50 to 100 mgs. Ra, the original lilac color vanishes and the crystal after twenty-four hours' radiation is almost white, which may be due to color compensation by the green color being produced. In two days the green color is well developed and reaches a maximum about the third day, approaching an emerald green, though somewhat lighter. The color is readily restored to lilac, either by light or by heat, and by ultra-violet light in remarkably short time. The cycle can be repeated indefinitely, apparently without fatigue. Fluorescence under penetrating or alpha radiation is of a characteristic orange-yellow or salmon-yellow, and less brilliant phosphorescence has been observed for more than a month after cessation of radiation. In the long duration of phosphorescence it resembles calcite as well as in the color of the phosphorescent light. In thermophosphorescence kunzite exceeds all of the other minerals hitherto examined. Well below 100° C. the intensity of light becomes much enhanced, at 125° it becomes a bright yellow, and at 200° a watch dial is well illuminated by the light from a small crystal. If raised rapidly to 250°, the light is very brilliant, but becomes exhausted rapidly at this temperature, and drops to a much lower intensity with a reddish hue. Apparently

simultaneously with exhaustion of most of the light, the original lilac color is restored. In fluorescence kunzite responds immediately to either penetrating or alpha rays from quite small quantities of radium and no marked change in fluorescence is observed as the coloring progresses.

From the standpoint of coloring, fluorescence and phosphorescence, kunzite is the most interesting of all minerals, and together with fluorspar and calcite forms a distinct class.

Calcite.—Different varieties of calcite showed the greatest differences in the properties of coloring, fluorescence, and of thermophosphorescence, which vary from complete absence to presence in marked degree. Through the kindness of Prof. William P. Headden of the Colorado Agriculture College, we have had an opportunity of observing some of the effects in special specimens of calcite which he had collected. Some of the varieties were colored yellow by 200 mgs. of Ra in the course of one to two months or by 150 millicuries of emanation in one to two weeks, when contained in rather large tubes. The fluorescence of certain samples is marked under the influence either of alpha or penetrating radiation. The color of fluorescence is a reddish orange and phosphorescence is very persistent at ordinary temperature. Professor Headden will describe his results for calcites in the *American Journal of Science*, to which reference should be had for a full consideration of the subject. The varying behavior of calcite is in marked contrast to the uniformity of kunzite as they came under our observation. The varieties of calcite which are active are quite comparable, however, with kunzite both in fluorescence and phosphorescence produced by radium radiation.

Sapphire.—Experiments have been carried out with 25 or 30 specimens of different colors and from various localities, including some synthetic ones. All specimens were uniform in exhibiting no fluorescence, either to penetrating or to alpha radiation. Thermophosphorescence was not observed in natural crystals, but was exhibited faintly by both white and pink synthetic crystals. The thermophosphorescence was characterized by the relatively high temperature at which it appeared (above 150° C.) and at which it persisted (350° for a pink synthetic crystal). At 350° it was more brilliant than kunzite which had passed its maximum at a lower temperature and had dropped to a much fainter intensity. The thermophosphorescence of syn-

thetic pink sapphire was red or orange-red, of synthetic white was yellow, which became paler with increasing temperature. Not a sufficiently large number of natural crystals was examined for thermophosphorescence to be sure that its absence is characteristic.

Change of color under radiation is general, but not universal. Colorless crystals either natural or synthetic are usually changed to golden or canary yellow in two to three days by the radiation from 200 mgs. Ra. Pink crystals either natural or synthetic were easily changed to a burnt orange color, probably corresponding to the addition of yellow to the original pink. Blue crystals change to a grayish or brownish-green, without beauty or brilliancy, but the original color can be restored either by light or heat. Light yellow is usually deepened to a canary yellow, but may take green shades instead, which latter may also result in some cases from colorless specimens. In no case observed was the color produced light-permanent, resembling in this respect rock salt, kunzite, and fluorspar.

Ruby.—The color changes in ruby are not marked. Light-colored natural ruby was not changed by radiation. Synthetic ruby was slightly darkened. Neither natural nor synthetic ruby showed any fluorescence under penetrating radiation, but showed a faint deep red fluorescence in emanation. Synthetic ruby showed a faint dark red thermophosphorescence at 150° C.

Emerald.—Neither natural nor synthetic emerald showed fluorescence under penetrating or alpha radiation; nor was change of color produced in any case. Synthetic emerald which had been exposed to 150 m.c. of emanation for ten days showed a faint green thermophosphorescence at 200° C.

Topaz.—Several different specimens of colorless topaz responded very uniformly to the penetrating rays from 200 mgs. Ra, though more slowly than rock salt, sapphire, and kunzite. In about a month a brownish amber color was produced which was uniform in all the specimens examined. Smoky topaz deepened in its own shade. The colors produced in topaz are apparently light-permanent. Neither fluorescence nor thermophosphorescence was observed.

Garnet.—Three specimens of deep red garnet acted uniformly in undergoing a reduction in color by the penetrating rays from 200 mgs. Ra, the color changing from deep red to violet, or

purple. The color change produced is apparently light-permanent. No fluorescence nor thermophosphorescence was observed.

Quartz.—A fairly large number of specimens of different varieties of quartz was examined. In most cases the smoky color, characteristic of some varieties of natural quartz, is produced by radiation either from an initial colorless or by deepening a light smoky color or by changing the amethystine or rose color to smoky. A few failures to produce any color in colorless quartz by 200 mgs. Ra in one month were encountered.

In some cases radiation of light amethyst deepens the amethystine color, in other cases it changes to the smoky color. Continued failure to produce amethystine color in colorless quartz suggested the following test: A crystal of amethystine quartz was decolorized by heating in air to a dull red. After cooling, it was exposed to the penetrating radiation from 200 mgs. Ra which gradually restored the amethystine color, and after several months carried it to a much deeper amethystine shade than the original. While quartz is not fluorescent, either under penetrating or alpha radiation, most specimens show a marked thermophosphorescence of bluish-white or bluish-green shade, which is quite persistent and equal in brilliancy to that of fluorspar. Other specimens of milky quartz and amethystine quartz showed no thermophosphorescence following radiation, though both were decolorized under heating.

Glass.—Since the publication of the previous paper on the coloring and thermophosphorescence of glass, some additional results have been obtained which will be described here.

At the suggestion of Professor Bancroft and Mr. Jerome Alexander, of the National Research Council, a rather detailed study was made of three slides of different thicknesses of decolorized gold ruby glass⁴ to see if restoration of ruby color could be observed and followed by the ultra-microscope, in an attempt to throw some light on the nature of the color and the supposed colloidal coagulating action of the radiation. As in a previous attempt,⁵ with much less satisfactory material, no ruby color

⁴ The slides used were prepared by the Corning Glass Works through the kindness of Doctor Sullivan, to whom we are greatly indebted. They were about the size of microscope slides, $\frac{1}{2}$, 1, and 5 mm., respectively, in thickness, were absolutely colorless, and splendidly prepared.

⁵ *Loc. cit.*, p. 441.

was produced. This time a brownish or amber yellow resulted (in conformity with Doelter's result) instead of the violet previously obtained. This seems to show conclusively that radium radiation does not develop the ruby color in decolorized gold ruby glass, but brings out the usual color characteristic of the glass exposed to the radium rays—violet, yellow, or brown, depending on some other property of the glass. Mr. Alexander's ultra-microscopic examination of the colored slides failed to disclose colloidal particles, although the radiations had been continued for several weeks until the amber color had become very marked in the two thick slides.

Specimens of special glass (paste), cut to resemble a diamond, gradually colored an amber-brown under penetrating radiation from 200 mgs. Ra. On exposure to diffused light it changed back to colorless almost as rapidly as rock salt, which is the first instance of the rapid bleaching of radium-colored glass by light that has come to our attention.

A piece of glass which had been colored violet by radium about six years ago failed to show any thermophosphorescence up to 300° C. This appears to confirm the theory advanced in the previous paper that the condition produced in glass by radiation which causes thermophosphorescence, slowly reverses itself even at ordinary temperature without affecting the color.

Obsidian.—The colorless variety usually is colored smoky by penetrating radiation, but occasionally fails to become colored. The light smoky variety deepens to black in the course of one to two months under penetrating radiation from 200 mgs. Ra. It resembles quartz in its behavior regarding coloring and was not tested for thermophosphorescence.

Tourmaline.—Two specimens of tourmaline, one pink and one green, showed no change in color under penetrating radiation. The green tourmaline failed to fluoresce or to change color in ten days' exposure to an initial quantity of 150 millicuries of emanation, and later failed to show any thermophosphorescence up to 300° C. The pink specimen was examined only with respect to coloring by penetrating radiation.

Diamond.⁶—More than thirty specimens of cut diamonds, supposed to represent the principal diamond fields of the world, varying in size from a fraction of a carat to ten carats and in

⁶ For fuller details, see paper by the same authors which will appear in a later issue of this JOURNAL.

color from colorless to yellow and caramel brown, were examined. Fluorescence under penetrating radiation from a very thin tube containing 60 mgs. Ra could not be detected. Fluorescent response to alpha radiation in the emanation tubes was universal and very sensitive. The color of the fluorescent light in emanation varied for different specimens from green to bluish-green to greenish-blue to blue without any regularity with reference to the color of the diamond itself. For the same specimen the color of fluorescence varied somewhat with conditions as to intensity of radiation and gas pressure in the emanation tube (perhaps the latter only as effecting the former). Fluorescence was also observed near a thin alpha-ray bulb containing emanation.

Prolonged exposure (one month) to *penetrating rays* from 250 mgs. Ra failed to produce any change in color in five yellow Cape diamonds of four to ten carats. But prolonged exposure (45 to 75 days) to *alpha radiation*, either directly in 10 to 50 per cent. RaCl_2 salt or in emanation, produced universally a green color, which deepened with time (or with intensity of radiation) through grass green to a dark sage green. These results confirm that of Sir William Crookes⁷ and met with no exception in all the more than thirty specimens treated. Colorless and yellow diamonds seem to take equally perfect green. Brown diamonds were off shade toward olive probably due to superimposed brown. The color is apparently light-permanent but can be discharged by heating to 450°C . for about an hour and in a shorter time at higher temperatures, or more slowly at lower ones. By interrupting the heating any intermediate shade of green can be obtained. The original color is finally restored by continued heating. The puzzling question as to the depth of the penetration of the colored layer, and the appearance in some specimens of "carbon spots" will be considered in the following paper devoted exclusively to the diamond.

Chrysoprase, opal and *other opaque minerals* showed no color change. This seemed to be a general characteristic of the opaque minerals. Upon heating chrysoprase after exposure to emanation, no light effects were observed, but a surface discoloration was produced which destroyed the natural lustre of the cut stone.

Aquamarine (light green), *zircon* (almost colorless), *peridot*

⁷ Sir Wm. Crookes, *Phil. Tr. Roy. Soc.*, **214A**, 433-45 (1905); *Sci. American*, Supplement No. 2270 (July 5, 1919).

(light green), and *moss agate* exhibited neither color change nor luminous phenomena. Aquamarine was exposed to penetrating radiation from 210 mgs. Ra for almost two years without changing hue in the slightest.

DISCUSSION OF RESULTS AND THEORY.

The foregoing observations make no pretense to completeness, but are rather intended to show the complexity of the phenomena exhibited by the various transparent minerals and gems with respect to coloring and the emission of fluorescent and phosphorescent light, and to illustrate the difficulties that are encountered in attempting to propose a satisfactory theory. One is confronted with a most confusing complexity of relations and almost every possible combination is met. On the one hand, we have minerals like aquamarine and peridot which show a negative behavior throughout toward the radium radiations, being neither colored nor excited to any light emissions. Again, at the other extreme, we have a few minerals like kunzite and fluor spar which always exhibit in marked degree the phenomena under consideration. Among different specimens of the same mineral, we also have all extremes of behavior from complete regularity to almost complete variability. Such variable behavior has generally been regarded and, in the opinion of the writers, is properly regarded as pointing to the presence in certain minerals of *impurities* which are mainly responsible for their behavior during and following radiation. In those minerals, on the other hand, where no irregularity of behavior is observed, one is forced to the conclusion that the phenomena exhibited are due to properties inherent in the mineral itself.

That the presence of impurities, sometimes in minute quantities, plays a rôle in a variety of phenomena connected with coloring and light emission has been known for some time. It has been recognized in the case of phosphorescent alkaline earth sulphides, in the fluorescent-phosphorescent zinc sulphides, in the natural coloring of minerals, in the color produced in minerals by radiation, in the triboluminescence of natural zincblend (which must contain iron or manganese to show triboluminescence), and in many other related phenomena. It is not the purpose of the present paper to discuss primarily the rôle played by these impurities, though reference will again be made to them. A complete

explanation of their action will probably not be found until much more is known about the exact mechanisms of the various effects.

Several theories have been proposed to explain coloring and the light effects. In all of the most recent ones the influence or concomitance of *electrical* phenomena is recognized. There has been no lack of confirmation of the general truth of such a relation. Röntgen⁸ recently published a very exhaustive study of the influence of light and other forms of radiation on the conduction of electricity through crystals, principally sodium chloride.

Lenard⁹ has investigated the effect of light on phosphorescent zinc sulphide from the standpoint of photo-electricity. Earlier Meyer and Przibram¹⁰ reported that minerals which had been colored by radium radiation exhibit enhanced photo-electric effects. Przibram¹¹ has further developed their original theory. There can then be little doubt that the phenomena depend primarily upon electrical effects produced in the minerals by radiation. It is also most natural to suppose that the light effects during subsequent heating are caused by the return of electrons to their original positions. Insofar the present writers can agree with the general theory.

The statement previously made by one of us,¹² based on the behavior of violet-colored glass that: "The mistake has been rather commonly made of supposing that there is a close connection between the discharge of color produced in glass, for instance, and thermophosphorescent effect," appears to have been slightly misunderstood by Przibram.¹³ It was not meant to imply that there is *no* connection between the two phenomena. We agree with Przibram that when a mineral exhibits both thermophosphorescence and decolorization by heat, usually the two phenomena are *apparently* coincident. We are inclined to believe that a more careful examination of this coincidence should be made before the statement can be made positively. The case of glass does appear to be exceptional, but the occurrence of even *one*

⁸ W. C. Röntgen, *Ann. d. Phys.* [4] **64**, 1-195 (1921).

⁹ P. Lenard, *Ann. d. Phys.* [4] **38**, 553-73 (1922).

¹⁰ St. Meyer and K. Przibram, *Sitzb. Akad. Wiss. Wien*, **123**, IIa, 653-63 (1914).

¹¹ *Ibid.*, **130**, IIa, 265-70 (1921).

¹² Lind, *Jour. Phys. Chem.*, **24**, 442 (1920); also "Chemical Effects of Alpha Particles and Electrons," p. 52.

¹³ *Loc. cit.*, p. 265.

such marked exception as that of glass, where the temperature of maximum thermophosphorescence and of decolorization differ by 200 to 300° C., should serve to make one very cautious in making any generality requiring that decolorization and thermophosphorescence coincide, and have an absolutely identical cause. Moreover, as shown in the present paper, and as is generally known, we have numerous cases of minerals in which one or the other of these two phenomena (coloring or thermophosphorescence) is lacking. For example, rock salt and sapphire, which are readily colored, show no visible light at the temperature of decolorization nor at any other temperature below incandescence. On the other hand, certain varieties of calcite, which show marked thermophosphorescence following radiation, are not colored by radiation at all. A more careful study of other minerals may disclose that even where both phenomena are exhibited they are not always coincident. It should be mentioned, however, that such coincidence does not appear to be essential to the theory of Meyer and Przibram any more than it is to the one which will be advanced in the present paper.

The principal point of departure of the different theories is in regard to what produces the color. In the theory of Meyer and Przibram the assumption was made that the primary effect of radiation is to furnish electrons which then neutralize positive metallic ions, giving neutral atoms of the metals. Coagulation (*Ausscheidung*) into colloidal particles then takes place which are responsible for the color. Meyer and Przibram support this theory by the similarity of colors produced in a series of synthetic alkali and alkaline earth borates to the colors found by Svedberg¹⁴ for the organic sols of the corresponding bases. Decolorization and accompanying thermophosphorescence are then caused merely by the reversal of this process under the stimulation of heat. The electrons liberated by the heat return to their original positions with the emission of light; the colloidal particles disintegrate, and the original color is restored. While the theory is a very elegant one, the present experiments appear to lend it little support. The efforts to reproduce by radiation the ruby color of gold-ruby glass which had been decolorized by heat, not only produced no ruby color, but produced no particles which could be recognized as colloidal in the ultra-microscope, although the usual colors of glass

¹⁴ T. Svedberg, "Die Methoden zur Herstellung Kolloider Lösungen," Dresden (1909), pp. 481 and 486.

(violet in one case and yellow in another) were produced. This seems to show that the colors produced in glass, and certainly in those minerals which are even more easily colored, are more readily brought about than is colloidal separation and cannot be attributed to the latter. In fact, the great ease with which some minerals are colored and the corresponding ease with which they are decolorized (even by diffused light of low intensity), leads us to look with disfavor on any theory involving the transport of masses of atomic size (or larger) through a solid medium.

The theory advanced by Newberry and Lupton¹⁵ is simpler than that of Meyer and Przibram. It involves only the assumption of primary ionization into a positive and a negative ion, both of atomic dimensions, one of which is capable of producing color and both of which remain separated by minute distances. Under stimulation of heat the ions recombine (with the emission of light) as in ordinary chemical reaction. While the objections to this theory are less formidable, nevertheless it appears to have been conceived more in conformity with the principles of ionization in electrolytic solutions and without any special reference to electronics or to crystal structure as revealed by the space lattice.

The following appeals to us as a simpler and more general theory.¹⁶ Certain groups of *electrons* are displaced by radiation from their normal positions and take up new metastable positions among the atoms. No displacement (or only secondary displacement) of the atom is involved. No change in the crystal lattice as revealed by X-rays would be expected nor would there be any production of colloidal particles. One or more groups of electrons may be involved. By *group* is meant a number of electrons all having uniform positions in the original atoms from which they are displaced and taking after displacement uniform new positions among the other atoms.

In cases where two or more groups are involved, the return of one group to the original position may cause thermophosphorescent effects, the return of a different group may cause decolorization. This does not preclude the possibility that a single group may bring about both phenomena, thus rendering them absolutely

¹⁵ *Loc. cit.*

¹⁶ The possibility of a theory based on a change in the mode of electronic "binding" (Bindungsweise) was mentioned in the earliest paper of Meyer and Przibram (*Sitzb. Akad. Wiss. Wien*, 121, IIa, 1416 (1912)), but was not further elaborated nor mentioned in their subsequent papers.

coincident. On the other hand, the possibility is evident that the two may be entirely independent, each having a different energy index or either one may be entirely lacking, as we have shown to be the case for certain minerals.

According to this theory the color might still be due to the positive ions. It appears to us, however, more probable that the color is due to the vibration of the electrons in their abnormal positions. G. N. Lewis¹⁷ has assumed the production of color in organic compounds by the vibration of electrons partially relieved of their constraints by a change in the surrounding electrostatic field so that they vibrate at a lower frequency which may fall in the visible region. He has shown that, owing to their small mass, electrons are more readily influenced as resonators than are atoms or ions. Our assumption is then that these electrons are removed by radiation to abnormal positions in which their constraints are lessened so that they vibrate with a frequency which may, and frequently does, fall in the visible region. Since the crystal is transparent the color complementary to the one absorbed by the electronic vibration is transmitted. In the metastable positions, under less constraint, the electrons are also freer to take part in electrical conduction and in photo-electric emission under radiative stimulus, and can also return to their normal positions under this stimulation or by that of heat.

Color-saturation would then be reached under continued radiation when the number of electrons returning to normal positions just equals the number being displaced. Upon cessation of radiation the electrons in abnormal positions may either remain indefinitely in the metastable position or may return gradually to their normal positions. The latter action will be brought about more rapidly by the stimulation of heat or some form of radiation of sufficient intensity to displace electrons from their abnormal positions without causing others to be driven from normal positions. One set of electrons may slowly revert, while another set remains indefinitely displaced. This is apparently the case in violet-colored glass where the power to thermophosphoresce gradually disappears even at ordinary temperature while the color persists undiminished. At about 200 to 300° C. the former action becomes very rapid and is complete in one-half to one hour, while the color is not discharged below 450 to 500°.

¹⁷ G. N. Lewis, *Chem. Met. Eng.*, **24**, 871-5 (1921).

The influence of impurities, in the light of this theory, may be one or both of the following: (1) To loosen electrons so that they are more readily displaced. Again this effect may be due (a) to an effect exerted only on the electrons of the original atoms, or (b) by the formation of complexes from which the electrons are more readily displaced than from normal atoms. (2) The influence exerted by the impurities may be exerted on the electrons after liberation, in holding them more firmly in the abnormal positions, or both (1) and (2) may act jointly in some cases. The presence of an impurity may not be essential in all substances to the electronic displacements under consideration.

Although this theory may be more comprehensible when considered in the light of the atomic structure in a crystal lattice, a crystalline or lattice structure is evidently not essential, as illustrated by the behavior of glass. It is evident that a crystal structure is not regarded by Lewis as essential to his electronic theory of color, since he extended it to the color produced by the reaction $\text{N}_2\text{O}_4 = 2\text{NO}_2$.

It is also evident that one would not expect the phenomena under discussion to be exhibited by any but transparent minerals. It is shown in the present paper that opaque minerals do not show any color changes under radium radiation. It may also be pointed out that those minerals which have intrinsic color (Doelter's "Eigenfarbig") are usually opaque minerals, while those which have no intrinsic color, which show variety of color in nature and are subject to coloring by radiation, are all transparent minerals.

We can find in the present results very little support for the theory that colored minerals in nature have been colored by the action of the earth's radioactivity. If this were the case for diamonds, for example, we should expect to find in nature many *green diamonds*, since this has been shown to be the commonest (and in our experiments the only) color produced by radium radiation; but actually *green* is a very rare color in natural diamonds. (See paper on the diamond which will appear in a later issue of this JOURNAL.) Furthermore, the artificial colors, even when similar to the natural ones, appear to be much less permanent with respect to heat and often with respect to light.

On the basis of the present theory the actual proportion of color-producing electrons to the total number of atoms in a given slightly colored mineral must be quite small. It is calculated from

ionization by penetrating radiation that the fraction in rock salt just noticeably colored is of the order 10^{-5} . Accordingly the quantity of energy necessary to produce (and even more so to discharge) color is surprisingly small in some cases. In general, it may be stated that the colors which are most easily produced are also most easily discharged and *vice versa*.

While it may be objected that the theory here proposed is not very definite and has not been quantitatively supported, it appears to us that it is capable not only of explaining the phenomena under consideration, but also has the necessary elasticity to fit the various other phenomena which are encountered and which must be explained. A more quantitative support must await a more intimate knowledge of atomic structure and of the properties of electrons and ions within that structure.

It is a pleasure to express our indebtedness for valuable assistance and suggestions and for the loan or gift of experimental material to: Prof. W. D. Bancroft and Mr. Jerome Alexander, of the National Research Council; to Doctors Hull and Davey, of the General Electric Company; to Professors Jones and Lincoln, of the University of Nevada; to Professor Headden, of the Colorado Agriculture College; to Mr. E. F. Holden, of the University of Michigan; to Mr. J. B. E. Bell, of Reno; to Mr. R. G. Monroe, of New York, and to the Corning Glass Company, of Corning, New York, and to the American Gem Mining Syndicate, of St. Louis.

The Effect of Long Grinding on Quartz. R. C. RAY. (*Proc. Roy. Soc., A* 718.)—"It has been shown from determinations of the heats of solution that when silver sand is subjected to grinding for a long time in a mechanically operated agate mortar, it partially loses its crystalline structure and is converted into the vitreous state." As there is a considerable difference between the densities of quartz and silicon glass it seemed worth while to see whether grinding affects density. Unground silver sand had a density of 2.638 gr. per cu. cm.; after grinding for fifteen hours it sank to 2.528, while silicon glass gave the value 2.208. From the amount of the change it appears that 25.7 per cent. of the sand was converted into the vitreous state, while from the change in the heats of solution the corresponding percentage was 31.2.

Other investigators have found that grinding diminishes the density of crystalline lead oxide, but fails to produce such a change in the amorphous oxide.

G. F. S.

ON THE PHOTOGRAPHIC INTENSITY OF FLASHLIGHT MATERIALS.*

BY

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PHOTOGRAPHIC literature contains an abundance of information relative to certain scientific phases of flashlight photography. The major portion of this literature deals with the chemical content of the flash materials with descriptions of apparatus for the discharge of such materials. It is the purpose of this paper to present information of another nature, that of the photographic intensity of flash materials.

A problem of this type necessarily involves considerable experimental data, and due to the great variety of flash materials available two were selected whose use is widespread, while a third was included as a possible means of corroborating the evidence of one of the others. In a photographic problem the choice of photographic materials is highly important, especially so when the material used is the medium by which intensity values are to be determined.

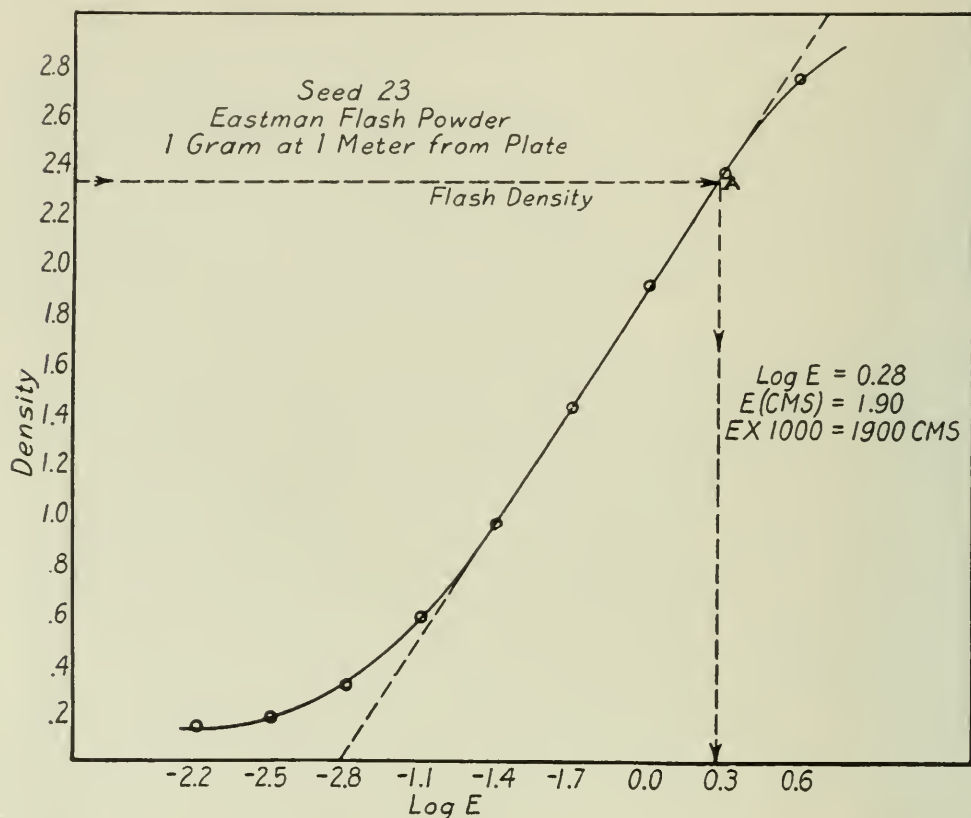
The flash materials used in this work were Eastman Flash Powder No. 3, magnesium powder, and magnesium ribbon, while the photographic materials consisted of Seed 23, Standard orthonon, and Wratten and Wainwright panchromatic plates. Each flash material had its intensity value determined on each of the three photographic materials.

Eastman Flash Powder contains magnesium and other metallic powders and substances which act as accelerators of its combustion. This powder is highly combustible and instantaneous in its action. An apparatus was constructed for the electrical discharge of the powder, each discharge firing one gram. This was accomplished by using nichrome wire between the terminals from the source of electrical supply, the wire being filed thin where it passed into the discharge container.

* Communicated by Dr. C. E. K. Mees, Director of the Laboratory and Associate Editor of this JOURNAL. Published as Communication No. 189 from the Research Laboratory of the Eastman Kodak Company.

The magnesium powder was discharged in an especially designed blow lamp readily obtainable commercially. In this lamp the powder is blown up through an aperture around which is a wick burning alcohol. In this manner it was possible to burn

FIG. 1.



a given weight of powder rather completely. Again each charge contained one gram of powder.

The tests with magnesium ribbon consisted merely in burning one gram of it directly in front of and at a metre's distance from the photographic plate.

The values of photographic intensity were obtained sensitometrically. By means of an instrument described by L. A. Jones,² portions of the photographic plate to be tested were exposed and then developed with a flash exposure made with one of the flash materials on another portion of the same plate. It is very important to note at this point that the strips made in the sensitometer

² Jones, L. A., "New Non-Intermittent Sensitometer," JOUR. FRANK. INST., March, 1920.

were exposed to an acetylene flame screened with a Wratten No. 79 filter, producing light of daylight quality. Therefore, the values given in this paper are visual candle-power-seconds of screened acetylene. After completion of the development processes, the characteristic curve of the plate was obtained and on it was marked off the density obtained by the flash exposure. Fig. 1 illustrates the method used. The flash density A is marked off on the curve and projected to the $\log E$ axis. The value determined from this point is in metre-candle-seconds, the sensitometric standard exposure notation. This metre-candle-seconds value is numerically equal to the candle-power-seconds value for the light source used, since all exposures were made with the light source at one metre from the photographic plate. The values given in the various tables are therefore in terms of candle-power-seconds. No attempt was made to determine the duration of the flash in the various cases, and it is therefore impossible to separate the candle-power-seconds value into its component parts, time and intensity. Some information relative to the duration of the flash of flashlight materials is contained in a paper by J. I. Crabtree.³

Since the intensities of the flash materials were so great and as it was desirable to use one gram (a small, easily measurable, quantity) of each material at one metre from the photographic plate, a piece of carefully selected, visually neutral film with a density of 3.0 (transmission .001) was placed directly in front of the photographic plate during each flash exposure. Although neutral film is not recommended for photographic work due to a lack of photographic neutrality, its use was considered permissible in this case. Tests made without the neutral film, using very small quantities of flash material, showed that the ratio of the results obtained agreed very well with those obtained with the neutral film. The candle-power-seconds values as obtained from the curves were of necessity multiplied by 1000—the factor of the neutral film used. The following tables contain the results obtained in each of the above-stated cases. The values given are the number of visual candle-power-seconds of screened acetylene to which one gram of the various materials is equivalent when evaluated in terms of the photographic material indicated.

³ Crabtree, J. I., "The Nature and Speed of Flash Powders," *Brit. Jour. Phot.*, January, 1917.

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TABLE I.
Candle-Power-Second Values.

Set.	Ordinary Seed 23.	Ortho.romatic Standard Ortho.	Panchromatic W. and W. Pan.
<i>Eastman Flash Powder.</i>			
1	1800	1100	1500
2	1800	1250	1300
3	2200	1200	1400
	—	—	—
Mean	1900	1200	1400
Ratio	1	.6	.7
<i>Magnesium Powder.</i>			
1	2300	4600	8000
3	2300	4500	7500
	—	—	—
Mean	2300	4600	7700
Ratio	1	1.9	3.3
<i>Magnesium Ribbon.</i>			
1	2500	4100	4500
2	2700	4900	5500
3	3400	5400	6600
	—	—	—
Mean	2850	4800	5600
Ratio	1	1.7	2.0

The various samples of powder and ribbon used were very carefully weighed and every precaution taken to obtain reliable photographic results. All plates were developed for three minutes in laboratory pyro at 68° F.

Examination of the above results shows that the photographic intensity of the flash powder is greater when determined on ordinary (blue sensitive) materials than when the orthochromatic and panchromatic materials are used. The reverse is true in the case of magnesium powder and magnesium ribbon. It will be noticed also that the values obtained with the pure magnesium are higher than those obtained with flash powder. This is especially true in the case of intensity values evaluated in terms of panchromatic materials. An examination of the spectra of the various materials shows differences due to the presence of metals other than magnesium in the flash powder. The presence of these materials tends to give a larger proportion of radiation in the region of shorter wave-lengths. This may be considered as partly

responsible for the higher relative photographic intensity of this material as determined on ordinary photographic materials. It is also probable that the presence of the accelerating agent causes combustion to take place much more rapidly and at a higher temperature in the case of flash powder than with magnesium powder and magnesium ribbon. This higher temperature also tends to cause a greater portion of the energy to be radiated at the shorter wave-lengths. The flash powder gives therefore a relatively bluer light than the magnesium powder and magnesium ribbon, the result being that the intensity values of the flash powder are higher when measured with ordinary materials. The reverse is the case with magnesium and is due to a preponderance of radiation in the region of longer wave-lengths.

For council and advice in procuring the above data, I am greatly indebted to Mr. L. A. Jones and for experimental assistance my acknowledgments are due Mr. R. F. Fisher, both of this laboratory.

Methyl Red.—This compound is used as an indicator in titrations and for the colorimetric determination of hydrogen ion concentration. It is paradimethylaminoazobenzene-orthocarboxylic acid and forms violet crystals. Its hydrochloride forms steel-blue crystals. Both types of crystals must be dissolved in alcohol to obtain the reagent. A. W. SCHORGER (*Ind. Eng. Chem.*, 1923, xv, 742-743) has studied the synthesis of methyl red, and has prepared its sodium salt as reddish-brown crystals. These crystals are soluble in water; and the resulting solution may be used as a reagent. J. S. H.

Phenol-Chlorine Water Pollution.—According to EDWARD F. KOHMAN, of the Research Laboratory of the National Canners Association (*Ind. Eng. Chem.*, 1923, xv, 518), a medicinal taste in canned peas and pears was shown to be due to the use of river water which had been contaminated by the effluent from a coke plant, and had subsequently been chlorinated for use as a municipal water supply. This type of pollution has recently been noted in the water supply of several American cities. Chlorination imparted the pronounced characteristic taste to water containing 1 part of phenol in 750,000,000. The taste, which is attributed to the formation of a dichlorophenol other than 1, 2, 4 dichlorophenol, or else to the formation of an entirely new compound, was destroyed by an excess of chlorine. The taste was accompanied by a penetrating odor, and developed only at high dilutions. If phenol was present in concentrations greater than 1 part in 50,000,000, only the characteristic phenolic taste of the common chlorphenols was obtained on chlorination. J. S. H.

The Separation of Elements into Isotopes. (*Phys. Rev.*, March, 1923.)—It is no longer a question whether this is possible in the case of mercury. The problem is to do it most quickly and economically. At the meeting of the American Physical Society in the last days of 1922 two papers on this subject were presented from the University of Chicago. R. S. Mulliken reported on a combined evaporation and molecular diffusion method. The mercury is evaporated from a 500-c.c. flask at the rate of 500 c.c. per hour. Of this 80 c.c. diffuses, the remainder condensing and running back into the flask. Since it is the lighter molecules that will evaporate in the greater proportion and that will later diffuse most, the liquid remaining in the flask constantly increases in density. "A spread of 0.1 unit has now been obtained."

W. D. Harkins and S. L. Madorsky at the same meeting described a steel vacuum apparatus that gives a separation of .1 unit in the atomic weight after a run of 180 hours combined with the operation of a smaller still for twenty-five hours. The method is one of evaporation alone. The vapor from the liquid meets a steel ceiling, collects into drops and runs away. This resulting liquid is always .005 unit lighter in atomic weight than the liquid left behind. The operation of the apparatus is automatic after the process has begun except in so far as the addition of mercury and the removal of samples is concerned.

The above experiments came from the University of Chicago. From Columbia University James Kendall reports three additional methods as being tried out for elements other than mercury. "It is possible that in an extreme case such as Li^6 and Li^7 an appreciable difference in the points of fusion of the pure isotopes will exist, and so permit a separation by fractional distillation." Two different methods are being used in an endeavor to separate Cl^{35} from Cl^{37} . According to Nernst's e.m.f. equation the discharge potentials of these should differ by .03 volt. It may, therefore, be possible to separate them by "electrolytic fractionation." Mercury, magnesium and lithium are likewise under examination by this method.

The second chlorine method is this. "An agar-agar gel containing chloride is inserted as a short middle section in a long horizontal tube, being preceded by a gel containing a faster anion (hydroxide ion) and followed by a gel containing a slower anion (acetate ion). When a current is passed, the boundaries between the solutions remain perfectly sharp as the chloride moves slowly toward the anode. New tubes of hydroxide gel are inserted before it reaches its goal, and after it has travelled (say) 100 feet the chloride gel is sectioned and analyzed. If Cl^{35} and Cl^{37} ions possess different mobilities, the front sections should contain only the one isotope, the rear sections only the other. . . . The importance of the application of this method to the separation of the metals of the rare earths, saving the laborious recrystallizations at present necessary, should be noted."

G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

SOME COMPRESSIVE TESTS OF HOLLOW TILE WALLS.¹

By Herbert L. Whittemore and Bernard D. Hathcock.

[ABSTRACT.]

THE Bureau of Standards has published the results of tests of hollow building tile in its Technologic Paper No. 120.

As the strength is important when built into a wall, similar tile were used in constructing thirty-two walls each 4 feet long, 12 feet high, and either 6, 8, or 12 inches thick.

The work was done in coöperation with committee C-10 on hollow building tile of the American Society for Testing Materials.

The National Fire Proofing Company donated all the tile, which were of such design that all the net area was in bearing when carefully set on end in the wall.

As the strength of these tile was greater than the strength of the average tile used in buildings, the results of this investigation should be used with discrimination.

The mortar was 1 cubic foot of Portland cement, $\frac{1}{4}$ cubic foot of hydrated lime, and 3 cubic feet of sand dried in an oven.

The walls were laid with great care by an experienced mason, and were of much better workmanship than is usually obtained.

The walls were, with a few exceptions, tested when one month old.

After placing the wall in the testing machine, it was capped with plaster-of-Paris, the upper head brought into contact with the wall, and the cap allowed to set for twelve hours or more.

Compressometers were placed at each corner, and readings taken during the test. Stress curves were drawn to show the behavior of the walls. Strain-gauge readings were also taken both on the tile and across the horizontal joints. Due to the great differences in the modulus of elasticity of the tile and the lack of data on the modulus for the particular tile on which strain-gauge readings were taken, these readings were of little use.

* Communicated by the Director.

¹ Technologic Paper No. 238, price five cents.

The horizontal deflections of the walls were measured at mid height of the walls.

The following conclusions may be drawn from the results of the test:

(a) Although the strength of the individual tile in lot A was about twice that for the tile in lot B, the strengths of the walls made from these tile were only slightly greater.

The ultimate strength of the walls made from the A tile averaged about 37 per cent. of the strength of the individual tile, while those made from the B tile averaged about 55 per cent.

(b) From the theory of columns, it might be expected that a thick wall, the height being the same, would sustain a greater load than a thin one. These tests, on the contrary, show no effects can be definitely ascribed to "column action," although the slenderness ratio for the 6-inch walls was over 60. This is confirmed by the small deflection of the walls.

(c) Apparently, there is no relation between the ultimate strength of a wall and the load at first crack.

(d) The walls having the cells of the tile vertical had, on the average, more than twice the strength of those having the cells horizontal. For both these cases, the values of the stress at failure were remarkably constant, being, apparently, independent of the size of the tile. The ultimate stresses computed on the net sectional area were also somewhat greater for the walls having the cells vertical, except for the 6-inch A tile, for which the stresses in the walls having the cells horizontal were slightly greater. Apparently, the advantage of setting the tile with the cells vertical is greater for eccentrically loaded walls than for walls which are axially loaded.

(e) In only one case could a direct comparison be made between "broken" and "unbroken" joints. Wall No. 31 with "broken" joints, but in all other respects identical in construction with walls Nos. 25 and 26, which had "unbroken" joints, shows a much higher strength. Conclusions, however, should not be drawn from the results from one specimen. Attention is called to the fact that in these tile the transverse webs were spaced to give full bearing over the end of the tile when the cells were vertical and the joints "broken," as well as when the joints were "unbroken."

(f) For the axially loaded walls, the failure was sometimes by crushing at the top and sometimes by vertical cracking through the joints. No consistent difference in strength was found for these two types of failure. Probably the crushing at the top was determined by the plaster cap which was somewhat weaker than the mortar joint.

(g) Walls loaded with an eccentricity of 2 inches over one-half the width of the wall had about one-half the strength of similar walls, axially loaded. Apparently, this ratio is independent of the thickness of the wall. The maximum deflection for the eccentrically loaded walls was, on the average, 0.04 inch, undoubtedly a very small value, which was exceeded by six of the axially loaded walls.

(h) Failure, in the case of the eccentrically loaded walls, was local. The upper bearing plate rested on two of the webs of each tile in the upper course. The stress in these webs was, therefore, much greater than in the lower courses in which the load was more uniformly distributed.

(i) The modulus of elasticity of the walls varied over a wide range, and, apparently, there is no relation between the modulus for the wall and that for the individual tile.

(j) Due to the wide variations in the moduli of elasticity of the tile and in the deformation of the joints it seems probable that failure of a tile wall is caused by the unequal distribution of the stresses. Therefore, any means of securing a more uniform stress distribution, such as selection of tile having the same physical properties, and setting them with a uniform thickness of joint would be expected to increase the strength.

Fish Meal as a Feedstuff.—Fish meal is a commercial product obtained by cooking, pressing and drying wholesome undecomposed raw fish material under sanitary conditions. JAMES B. MARTIN, of the U. S. Bureau of Animal Industry (*Jour. Asso. Official Agri. Chem.*, 1923, vi, 498-501), has studied the lard manufactured from hogs which had received fish meal as part of their ration. The fat of these hogs was identical with that of normal hogs in its physical aspects and ordinary chemical characteristics. However, the fat of the hogs which had received fish meal contained a small amount of the glyceride of clupanodonic acid, the characteristic fatty acid of fish oils.

J. S. H.

Nomenclature Rules Adopted by the Nomenclature Committee of the American Chemical Society and That of the London Chemical Society.—1. In naming a compound so as to indicate that oxygen is replaced by sulphur the prefix *thio* and not *sulpho* should be used (sulpho denotes the group SO_3H); thus, HCNS , *thiocyanic acid*; H_3AsS_4 , *thioarsenic acid*; $\text{Na}_2\text{S}_2\text{O}_3$, sodium *thiosulphate*; $\text{CS}(\text{NH}_2)_2$, *thiourea*. The only use of *thio* as a name for sulphur replacing hydrogen is in cases in which the sulphur serves as a link in compounds not suitably named as mercapto derivatives; thus, $\text{H}_2\text{NC}_6\text{H}_4\text{SC}_6\text{H}_4\text{NH}_2$, *thiobisaniline*. *Hyposulphurous acid*, not *hydrosulphurous acid*, should be used to designate $\text{H}_2\text{S}_2\text{O}_4$.

2. The word *hydroxide* should be used for a compound with OH and *hydrate* for a compound with H_2O . Thus, barium hydroxide, $\text{Ba}(\text{OH})_2$; chlorine hydrate, $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$.

3. Salts of chloroplatinic acid are *chloroplatinates* (not *platini-chlorides*). Similarly salts of chloroauric acid are to be called *chloroaurates*.

4. Hydroxyl derivatives of hydrocarbons are to be given names ending in *-ol*, as *glycerol*, *resorcinol*, *pinacol* (not *pinacone*), *mannitol* (not *mannite*), *pyrocatechol* (not *pyrocatechin*).

5. The names of the groups NH_2 , NHR , NR_2 , NH or NR should end in *-ido* only when they are substituents in an acid group, otherwise in *-ino*; thus, $\text{MeC}(:\text{NH})\text{OEt}$, ethyl *imidoacetate*; $\text{NH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, β -*aminopropionic acid* (not *amidopropionic acid*); $\text{NHPhCH}_2\text{CH}_2\text{CO}_2\text{H}$, β -*anilinopropionic acid*; $\text{CH}_3\text{C}(:\text{NH})\text{CO}_2\text{H}$, α -*iminopropionic acid*.

6. *Hydroxy-*, not *oxy-*, should be used in designating the hydroxyl group; as *hydroxyacetic acid*, $\text{CH}_2(\text{OH})\text{CO}_2\text{H}$, not *oxyacetic acid*. *Keto-* is to be preferred to *oxy-* to designate oxygen in the group —CO— .

7. The term *ether* is to be used in the usual modern acceptance only and not as an equivalent of *ester*.

8. Salts of organic bases with hydrochloric acid should be called *hydrochlorides* (not *hydrochlorates* nor *chlorhydrates*). Similarly *hydrobromide* and *hydriodide* should be used.

9. German names ending in *—it* should be translated *—ite* rather than *—it*; as *permutite*. If it seems desirable to retain the original form of a trade name it should be placed in quotations, as “*Permutit*.” Alcohols such as *dulcitol* (German *Dulcit*) are exceptions.

10. German names of acids should generally be translated by substituting *—ic acid* for “*—säure*.” Some well established names are exceptions, as *Zuckersäure* (*saccharic acid*), *Milchsäure* (*lactic acid*), *Valeriansäure* (*valeric acid*), etc. When the names end in “*—insäure*” the translator may substitute *—ic acid* unless another acid already bears the resulting name; thus, *Acridinsäure*, *acridic acid*, but *Mekoninsäure*, *meconinic acid*, because *meconic acid* (*Mekon-säure*) is different. Names ending in “*carbonsäure*” are to be translated *—carboxylic acid* (not *—carbonic acid*).

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

ADSORBED MOISTURE AND WATER OF CRYSTALLIZATION
IN CERTAIN COMMON DYES.¹

By H. Wales and O. A. Nelson.

[ABSTRACT.]

VAPOR pressure-water content curves have been obtained for methylene blue, crystal violet, erythrosin, magenta and tartrazin, for the purpose of determining whether the water present in these dyes is adsorbed or held as water of crystallization. Crystal violet and tartrazin alone show hydrate formation. Further proof was obtained that the equivalent of one molecule of water in erythrosin is present as part of the molecule and a new theory of the structure of this dye is offered.

EMULSIONS OF MINERAL OIL WITH SOAP AND WATER:
THE INTERFACIAL FILM.²

By Edward L. Griffin.

[ABSTRACT.]

IN an emulsion of mineral oil with soap and water, part of the soap is hydrolyzed, the fatty acids being dissolved by the oil droplets and the alkali remaining in aqueous solution.

Fatty acids may be kept from dissolving in the oil by the addition of excess alkali.

Part of the soap forms unimolecular films around the oil droplets. The average areas occupied by each molecule of sodium oleate, potassium stearate and potassium palmitate were 48, 27, and 30×10^{-16} sq. cm., respectively. These areas agree rather closely with those found for the corresponding fatty acids in unimolecular films on the surface of water.

In case there is insufficient soap to form a unimolecular film the emulsion is not stable.

The excess soap remains in water solution.

* Communicated by the Chief of the Bureau.

¹ Published in *J. Am. Chem. Soc.*, **45** (July, 1923) : 1657.

² Published in *J. Am. Chem. Soc.*, **45** (July, 1923) : 1648.

EQUATIONS FOR VAPOR PRESSURES AND LATENT HEATS
OF VAPORIZATION OF NAPHTHALENE, ANTHRACENE,
PHENANTHRENE, AND ANTHRAQUINONE.³

By O. A. Nelson and C. E. Senseman.

[ABSTRACT.]

EQUATIONS for vapor pressures and latent heats of vaporization of naphthalene, anthracene, phenanthrene, and anthraquinone were calculated by applying the Clapeyron equation of state. The entropy of vaporization of these compounds was also calculated and the conclusion that they all form normal liquids was reached. The vapor pressure observed for each compound agrees closely with the calculated pressure.

CHANGES IN POWDERED ROSIN STORED IN
CLOSED CONTAINERS.⁴

By F. P. Veitch and W. F. Sterling.

[ABSTRACT.]

SOME of the so-called constants of powdered rosin undergo pronounced changes within a short period of time, even when the rosin is stored in partially filled corked bottles. While the rate of change diminishes greatly after the first week, it continues at a significant rate for at least three weeks. At the end of six weeks the following changes had occurred: The acid number had decreased 5.3 to 9.3 points and the iodine number 47.3 to 52.2 points; the saponification number had increased 5.1 to 8.9 points and the melting point 8.9 to 11.3 degrees.

Obviously, therefore, samples of powdered rosin should not be prepared for analysis until the analysis is to be made.

Ferric Hydroxide as an Antidote for Arsenic. HORATIO C. WOOD (*Jour. Amer. Pharm. Asso.*, 1923, xii, 482-483) strongly defends the use of ferric hydroxide as an antidote in arsenic poisoning. Ferric hydroxide forms a relatively insoluble compound with arsenic, and thereby greatly retards the absorption of the latter. The insoluble compound is removed from the stomach by the vomiting which is an almost constant symptom of arsenical poisoning, or by the administration of emetics and laxatives. J. S. H.

³ Published in *Ind. Eng. Chem.*, **15** (June, 1923) : 621.

⁴ Published in *Ind. Eng. Chem.*, **15** (June, 1923) : 576-577.

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BOOK REVIEWS.

CHEMISCHE TECHNOLOGIE DES STEINKOHLENTEERS MIT BERÜCKSICHTIGUNG DER KOKSBEREITUNG. By Dr. R. Weissgerber. 8vo, vii-139 pages, illustrations and index. Leipzig, Otto Spamer. Price, paper bound, \$1.10 net.

The author of this work, a director of one of the German plants for producing and utilizing tar, has had a large experience in practical and analytical work. A thorough account is given of the present methods of differentiating the several important constituents of the crude tar. No one need be told that Germany has developed such industries to the highest point. Theodore Weyl, of Berlin, in the preface to his work on the "Sanitary Relations of the Coal-Tar Colors," said, "Thanks to the coöperation of theory and practice, the coal-tar color industry has conquered the world." The conquest has not been fully maintained of late years, for several of the nations which were joined against Germany have secured what may, in the terminology of the peace treaty, be called a mandate over some of the field, efficient plants for manufacturing coal-tar derivatives having been established in those countries.

A most interesting and valuable section of the work is that devoted to "low-temperature coking." We are not astonished to learn that this procedure was first applied in England. The same old story recurs often in the history of tar-technology, and, indeed, in other technologic lines. The first synthetic color was made in England, and it was Davy who first described the catalytic action of platinum on a mixture of sulphur dioxide and oxygen. The latter principle is now widely applied in the manufacture of sulphuric acid, but the details were worked out in Germany. The submarine and airplane are primarily American inventions, but it was left to Germany to demonstrate their use in war, and to bring them to a high degree of efficiency.

Low-temperature coking consists in distilling at not above 700°C., or somewhat below that point. The method was first applied in England to cannel coal, but the investigation of the fixed and volatile products was not pursued. Boernstein in 1906 found that coal began to emit gas at about 390° and between 400° and 500° yielded a tar that was quite different from that obtained by the ordinary high-temperature method. French and English investigators pursued the subject and obtained among other results special forms of volatile products by distilling under very low pressure. It was also found that the tar from the low-temperature process can be converted into high-temperature tar by transmission through red-hot tubes. During the war, the German coal-tar and coking plants studied the procedure extensively. Notwithstanding the interest that has been aroused in this matter and the promise of new and useful products, the low-temperature coking industry is still but slightly developed.

In the low-temperature distillation of coal, considerable amounts of water pass over, but this is not appreciably ammoniacal. The nitrogen remains in great part in the coke. The gaseous portion contains a large amount of methane, but comparatively little of the olefin group or of free hydrogen. Burgess and Wheeler published a comparative table of the products of distillation of a sample of coal at 1100° and below 600°. The contrast in ingredients is marked. Fischer and Glaud gave comparative figures of the composition of samples of low-temperature and high-temperature cokes respectively from the same coal. The

most notable difference is in the content of hydrogen and nitrogen, the low-temperature coke containing far higher proportions of these than that produced at high point. Low-temperature coke burns with a smokeless flame, and as it contains considerable hydrogen has probably a decidedly higher heating power than ordinary coke. Referring to heating power leads the reviewer to express regret that the author uses WE for this unit. This is an abbreviation of a German term, but it is not evident from the symbol alone whether the unit is commensurate with B.T.U. or one of the Calories. It is to be regretted that so much yet remains to be accomplished in unifying nomenclature and symbolism in science. Some German journals are now using the abbreviation v.H for percentage instead of the almost universal and briefer %. German chemists continue to use "benzol," "toluol" and so on for benzene and its homologues. By general consent "ol" now indicates an alcoholic structure.

The fact that the gas obtained from low-temperature coking contains a large proportion of methanes seems to indicate that it may afford a source of lighter fuel for motor vehicles, and thus relieve the strain on petroleum. The lack of olefins will give a low illuminating power, but the days of gas as a general illuminant may be over. Gases from coal will probably pass into very extensive use for heating and for stationary motors. Anything that will increase the profits of by-product coking will be of advantage to the comfort of human-beings, for the smokiness of modern cities certainly diminishes the enjoyment of life.

The greater portion of the book is devoted to the ordinary (high-temperature) coking, of which an exhaustive and valuable treatise is given. The procedures are largely illustrated and the nature and methods of refining the several fractions of the subsequent distillations are given in detail. Numerous references to the literature are given and in appropriate form, that is, the year and volume are both given when the periodical uses both, and the volume is indicated in full-faced type, so much more satisfactory and so much less liable to error than the Roman numerals.

The work will be of great value to gas and fuel engineers and chemists. The text is clear and exact and the mechanical execution of the book excellent.

HENRY LEFFMANN.

INTRODUCTION GÉOMÉTRIQUE A L'ÉTUDE DE LA RELATIVITÉ. By Henri Marais. 191 pages, 8vo, paper. Paris, Gauthier-Villars et Cie. Price 7 Francs 50.

The theory of relativity has attracted a great deal of interest in France since its presentation, and a very large amount of literature has appeared in response to this interest. French physicists and mathematicians are by no means unanimous on the subject, and while many publications endorse the theory earnestly, dissent is also expressed in equally positive form.

In the work in hand, the author proposes to present under simple yet intelligible form, a sort of grammar of the mathematical language of relativity, from the standpoint of geometry. Euclidean and Riemann conceptions of space are discussed and the laws of invariance for linear transformations of any type, indicating the function performed by geometric views in the theories of relativity thus explained. The book will interest both mathematicians and

physicists, and will be of special service to those who are familiar with the principles of analysis and desire to study a special exposition of relativity. Some difficulties generally encountered in studying the theory will be eliminated.

HENRY LEFFMANN.

LES ISOTOPES. By A. Damiens, D.Sc. ix-115 pages and contents, 8vo. Paris, Gauthier-Villars et Cie. Paper bound, 12 Francs.

It is well known that the theory that matter is discrete, the ultimate particle being infinitely small and incapable of reduction, was due to the early Greek philosophers. Their views are known to us only through quotations by later writers, and the theory was practically ignored for many centuries, until Dalton presented it in a form that was generally accepted in physical science. His suggestions led to great advances in chemistry, among which was Berzelius' system of symbols, which, being based on atomic weights, gave a quantitative value to all formulas. For about a century, the atomic theory in substantially its original form was generally accepted, but investigations began to show that while the atom may be considered the unit of chemical action, it is itself made up of minuter particles or foci of energy. The positive nucleus (proton) and the electron are now familiar terms. With the discovery of the radio-active elements there came a new concept, that of elements that have atomic weights so close that they occupy the same places in the periodic table but are not identical. It is not necessary to set forth the details of these discoveries. There is abundance of literature on the subject. The work of Doctor Damiens, now under consideration, is a clear and comprehensive summary of the methods of investigation and of the results that have been obtained in this field. While strictly scientific, the book is written in a plain manner, avoiding intricate mathematical data, and thus serves to inform the intelligent reader as well as the scientist. The work of investigators of all nationalities is presented clearly and fairly. Lavoisier's dictum, that an element is a substance of which the weight cannot be changed by the chemical actions which it undergoes, is no longer accepted. The idea of the molecule, indeed, came early into the view of chemists, but they regarded with comparative indifference the data that were being brought out by physicists. Notwithstanding the great changes that have been made in the atomic theory by the discovery of the complex nature of the atom, this is still the chemist's unit for all stoichiometric procedures.

A remarkable result of the discovery of isotopes has been the tendency to return to the hypothesis of Prout, who postulated the view that all atomic weights are simple multiples of the atomic weight of hydrogen. This was an attractive view, and was probably accepted more from sentimental than scientific motives, but the researches of Stas and Dumas rendered it untenable. Chlorine, especially, stood out conspicuously with an atomic weight almost exactly intermediate between 35 and 36. The development of the knowledge of isotopes among elements not radioactive has eliminated most of the difficulties of Prout's view, for by certain mixtures of isotopic forms with whole number atomic weights, a fractional weight of the element as it occurs is the result. Thus chlorine being shown to have two isotopes, of weights respectively 35 and 37, the fractional figure is explained. The table of isotopes

given in the book is taken from the recent report of the International Committee on Chemical Elements with the addition of data on antimony published since that report appeared. The array of numbers shows in several cases isotopes with identical masses, although not the same elements. Thus argon and calcium have each an isotope of 40, although it is not considered that these are identical substances. Similarly, selenium and krypton have isotopes of 80 and 78. The term "isobares" is applied to such coincidences, a word a little unfortunate, "isobar" being a term well established in meteorology. There seems, however, no other term that can satisfactorily express the idea, and if the spelling and pronunciation are preserved with the final "e" in the chemical term, little confusion will result.

Doctor Damiens' book can be recommended to all who wish to learn the methods and results of the investigations that have so profoundly modified the views as to the constitution of matter. One interesting point is that a possibility of multiple isomerism in inorganic compounds is foreseen. Hitherto organic chemistry has been almost exclusively the field for such conditions, but our author points out that if chlorine and potassium have each two isotopes and platinum six, one hundred and twenty-six isomers of potassium chloroplatinate are possible.

HENRY LEFFMANN.

CHEMISCH-TECHNISCHE VORSCHRIFTEN. By Dr. Otto Lange, Technical High School, Munich. Third edition, enlarged and thoroughly revised. Vol. I, Metals and Minerals. xxxvi-971 pages and index, 8vo. Leipzig, Otto Spamer. Price \$8 net.

This work, now issued in a third edition, is to be complete in four volumes. The volume in hand comprises metals, alloys and products therefrom. The second volume will cover textiles, artificial and natural in the broadest sense; the third, oils, fixed and volatile, soaps, laquers, colors, water and sewage problems; the fourth, fertilizers, food and feed-stuffs, explosives. The treatment of all the subjects is comprehensive and extensive. Analytical data are not included, reference being made to works specially devoted to such matters. The author has been able to include a large amount of information by frequent reference to the literature, so that any one desirous of pursuing more intimately a given investigation can follow up the details in many directions. Especially valuable is the thorough reference to the patent literature of the more important nations. This is, of course, a prominent feature of technology, though a very large portion of such literature is disappointing, patent-office officials being often not very discriminating as to the merits or originality of claims filed. The French "reservation" "s.g.d.g." might well be added to all issues.

Chemical technology, says Doctor Lange, rests upon the knowledge of the principles of chemistry; it aims to follow the processes of nature, but to hasten or delay these, and changes raw materials into forms that are useful to mankind. Its purpose is purely practical, but its proper development cannot be secured without the assistance of the pure science, the search for truth for truth's sake. Tradition and recorded history inform us that man began very

early to manipulate the materials found in nature, but the beginnings of some of our most important and familiar industries are lost in the mist of antiquity. The cave-man, who decorated the caves of western Europe with remarkable paintings, and who engraved pictures of animals on bones and tusks, seems to have developed the making of both vegetable and mineral colors although, it is true, many of these materials are practically ready formed in nature. It is interesting to note that perhaps the beginnings of civilization may have been due largely to women. In the earliest period when human-beings lived mostly in enmity with each other except within the kinship, the man was occupied in hunting animal food or defending his family; the woman remained at home to take care of the children. It was probably her attempts to raise grain and other vegetables that led to a change from a nomadic to a stationary life, the first step in civilization. Her efforts at spinning and weaving led to the substitution of textiles for skins for garments, and it is likely that the first rude pottery was from her hands. The occurrence of some few metals in the free state, and the comparatively easy reduction of others, led to early development of metallurgy, though it is generally held by anthropologists that stone implements for domestic use and for hunting and war preceded the employment of metals. The Odessey mentions the hardening of steel by immersion of the heated mass in water, specifically describing the preparation of the battle-axe.

We live to-day in an industrial civilization. Historians speak of the civilizations of the past, Egyptian, Babylonian, Greek, Jewish, Roman, but these had only limited resemblances to our modern life. In the basic impulses of human nature, of course, the story is the same, but to-day the problems socially and scientifically are industrial, and chemistry comes into play throughout the field. It is also the dominating science in the medical field, for physical chemical principles and methods are now almost entirely the basis of theories in biology and hygiene. To this industrial physio-chemical age, therefore, the book in hand appeals. It is indispensable to the worker, whose name is now "Legion," in the laboratory or in the direction of the factory. All these will find it a most serviceable and satisfactory guide. The amount of material here collected and arranged is immense. No narrow nationalism has restricted the scope of Doctor Lange's search. The war, as might be expected, has interfered with some verifications, but these relate to certain data in regard to location of patent literature. Yet in view of this comprehensiveness of reference it is at first somewhat puzzling to note from the list of periodicals consulted, the absence of such important ones as the *Journal of the Society of Chemical Industry* and the *Journal of Industrial and Engineering Chemistry*, also that no French journals are listed. The explanation is that for a large part of the non-German literature, reliance has been upon the abstracts in the German periodicals. That the non-consultation of leading British and American periodicals in this field has not been due to war conditions is shown by the fact that the *Journal of the Chemical Society* and the *JOURNAL OF THE FRANKLIN INSTITUTE* are enumerated as original sources. The use of abstracts is frequently unavoidable. German abstracts are usually comprehensive and trustworthy, yet it is somewhat unsafe to rely on secondary

sources. The extent of Germany's specialized literature in this field is shown by the enumeration of twenty-two publications under the title "Zeitschrift."

The book is divided into three main groups: A general discussion of metals, and their working, such as alloying, polishing, electrolytic deposition, etching and similar procedures; a special part in which the individual metals are described and their technology set forth, in which articles some history of the metal is given; a third section on mineral colors. It will be seen, therefore, that while the bulk of the work is on metallurgy, the scheme upon which it is based is so comprehensive that a large amount of accessory matter is included, and its usefulness as a work of reference thereby much enhanced. Use of the book is materially assisted by a good table of contents and an index of thirty-nine closely printed pages. The references are to paragraphs, not to pages, a fact of which the user is informed by a line on each page of the index. This method is useful when, as in the case, the text is closely printed, but it would be well to carry the paragraph numbers at the head of the page.

The work is a monumental summary of data in the field to which it is devoted, and gives an indication of the value the complete work will have. Doctor Lange deserves the thanks of the industrial chemist for his labor in this line, and the house of Otto Spamer deserves similar obligations for the manner and form of the publication.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 160, An Airship Slide Rule, by E. R. Weaver and S. F. Pickering, Bureau of Standards. Twelve pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This report describes an airship slide rule developed by the Gas-Chemistry Section of the Bureau of Standards, at the request of the Bureau of Engineering of the Navy Department. The development of this slide rule was requested by the Navy because of the successful results which had been reported of the Scott-Teed rule which had been developed and used by the British naval air service. It is intended primarily to give rapid solutions of a few problems of frequent occurrence in airship navigation, but it can be used to advantage in solving a great variety of problems, involving volumes, lifting powers, temperatures, pressures, altitudes, and the purity of the balloon gas.

The rule is graduated to read directly in the units actually used in making observations, constants and conversion factors being taken care of by the length and location of the scales. In order to simplify as much as possible the manipulation of the rule, absolute accuracy has in some cases been sacrificed to convenience. Generally this has been necessary only in those cases in which the data upon which the computations will be based are not subject to accurate observation.

It is thought that with this rule practically any problem likely to arise in this class of work can be readily solved after the user has become familiar with the operation of the rule; and that the solution will, in most cases, be as accurate as the data warrant.

Report No. 163, The Vertical, Longitudinal, and Lateral Accelerations Experienced by an S.E.5A Airplane While Manœuvring, by F. H. Norton and

T. Carroll. Five pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This investigation was carried out by the Langley Field Laboratory for the purpose of measuring the accelerations along the three principal axes of an airplane while it was manœuvring. The airplane selected for this purpose was the fairly manœuvrable S.E.5A and the instruments used were the N.A.C.A. three component accelerometer and the N.A.C.A. recording airspeed meter. The results showed that the normal accelerations did not exceed 4.00 g. while the lateral and longitudinal accelerations did not exceed 0.60 g.

Report No. 165, Diaphragms for Aeronautic Instruments, by Mayo D. Hersey, Bureau of Standards. Thirty-two pages, illustrations, plates, quarto. Washington, Government Printing Office, 1923.

In this report is presented an outline of historical developments and theoretical principles, together with a discussion of expedients for making the most effective use of existing diaphragms, and a summary of experimental research problems.

Flexible diaphragms actuated by hydrostatic pressure form an essential element of a great variety of instruments for aeronautic and other technical purposes. The various physical data needed as a foundation for rational methods of diaphragm design have not, however, been available hitherto except in the most fragmentary form.

Report No. 168, The General Efficiency Curve for Air Propellers, by Walter S. Diehl, Bureau of Aeronautics, Navy Department. Eleven pages, illustrations, quarto. Washington, Government Printing Office, 1923.

Report No. 168 is a study of propeller efficiency, based on the equation

$$\pi = \left(\frac{V}{\pi ND} \right) \cot (\varphi + \gamma)$$

where

V = speed of advance.

N = revolution per unit of time.

D = diameter of the helix described by the particular element under consideration.

$$\varphi = \tan^{-1} \left(\frac{V}{\pi ND} \right)$$

and

$$\gamma = \tan^{-1} \left(\frac{D}{L} \right)$$

It is shown that this formula may be used to obtain a "general efficiency curve" in addition to the well-known maximum efficiency curve. These two curves, when modified somewhat by experimental data, enable performance calculations to be made without detailed knowledge of the propeller. The curves may also be used to estimate the improvement in efficiency due to reduction gearing, or to judge the performance of a new propeller design.

Report No. 170, A Study of Longitudinal Dynamic Stability in Flight,

by F. H. Norton. Nine pages, illustrations, quarto. Washington, Government Printing Office, 1923.

This investigation was carried out for the purpose of studying experimentally the longitudinal dynamic stability of airplanes in flight. The airplanes selected for this purpose were a standard rigged VE-7 advanced-training airplane and a JN4h with special tail surfaces. The airplanes were caused to oscillate by means of the elevator, then the longitudinal control was either locked or kept free while the oscillation died out. The magnitude of the oscillation was recorded either by a kymograph or an airspeed meter. The results show that the engine speed has as much effect on the period and damping as the airspeed, and that, contrary to theory as developed for small oscillations, the damping decreased at the higher airspeeds with closed throttle.

PUBLICATIONS RECEIVED.

Chemisch-Technische Vorschriften. Ein Handbuch der speziellen chemischen Technologie insbesondere für chemische Fabriken und verwandte technische Betriebe enthaltend Vorschriften aus allen Gebieten der chemischen Technologie mit umfassenden Literaturnachweisen von Dr. Otto Lange. 3te, erweiterte und völlig neubearbeitete Auflage. I Band: Metalle und Minerale. 1011 pages, 8vo. Leipzig, Otto Spamer, 1923. Price, in paper, \$8; bound, \$9.

Les Isotopes. Par A. Damiens. Preface de M. Jean Perrin. 118 pages, illustrations, plate, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, 12 Francs.

Institute of Government Research. Service Monographs of the United States Government No. 26. The Bureau of Public Roads: Its History, Activities and Organization. By W. Stull Holt. 123 pages, 8vo. Baltimore, Maryland, The Johns Hopkins Press, 1923. Price, \$1.

La Relativité Vraie et la Gravitation Universelle. Par Georges Fournier. 130 pages, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, 7 Francs.

Chemische Technologie des Steinkohlenteers mit Berücksichtigung der Koksbereitung. Von R. Weissgerber. 141 pages, illustrations, 8vo. Leipzig, Otto Spamer, 1923. Price, in paper, \$1.10.

Introduction Géométrique à l'Étude de la Relativité. Par Henri Marais. 191 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, in paper, 7 Francs 50.

Canada, Department of Mines, Mines Branch. Summary report of investigations made by the Mines Branch during the calendar year ending December 31, 1921. 346 pages, illustrations, plates, maps, 8vo. Ottawa, King's printer, 1923.

La Simultanéité Générale et le Temps Universel. Par le lieutenant-colonel Corps. 20 pages, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, 3 Francs 50.

Red Telefonica de Guipuzcoa (España). Descripción, historia y estadística. Par el Ingeniero-Director de la Red D. Ignacio M. Echaide. 40 pages, illustrations, map, 8vo. Villafranca de Oria, 1923.

Comparison of Plante Type Secondary Batteries in Our and Foreign Countries in Respect of their Characteristics and Durability. Part I, Characteristics of Plante Type Secondary Batteries chosen for our first experiment.

By Sakae Makio, Electrotechnical Laboratory, Ministry of Communications, Japan. 37 pages, illustrations, plates, tables, diagrams, 8vo. Tokyo, 1923.

The Wind Factor in Flight: An Analysis of One Year's Record of the Air Mail. By Willis Ray Gregg and Lieutenant J. Parker Van Zandt. 15 pages, diagrams, quarto. Reprinted from *Monthly Weather Review*, March, 1923, 51:111-125. Washington, Government Printing Office, 1923.

National Advisory Committee for Aeronautics. Technical Notes No. 148, The Flexible Mounting of an Airplane Engine, by K. Kutzbach. 6 pages, quarto. No. 150, Notes on the N.A.C.A. Control Force Recorder, by H. J. E. Reid. 4 pages, photographs, quarto. No. 151, Tests on Built-up Airplane Struts having Initial Tension in Outside Fibres, by T. A. Schwamb and C. S. Smith. Abstracted by John G. Lee. 6 pages, illustrations, diagrams, photographs, quarto. No. 152, Thrust and Power Required in Climbing, by Georg Koenig. 19 pages, illustrations, quarto. Washington, Committee, 1923.

Royal Institution of Great Britain. Weekly Evening Meeting. Friday, January 16, 1920, Low-temperature Studies, by Sir James Dewar. 38 pages, illustrations, 8vo. Friday, June 10, 1921, Absolute Measurements of Sound, by Arthur Gordon Webster, D.Sc. 7 pages, illustrations, 8vo. Friday, March 3, 1922, Microscopic Parasites and their Carriers, by C. Morley Wenyon, C.M.G. 19 pages, illustrations, 8vo. Friday, June 2, 1922, Gilbert and Sullivan, by Hon. Maurice Baring. 14 pages, 8vo. Friday, February 23, 1923, The Interior of a Star, by A. S. Eddington, F.R.S. 15 pages, 8vo. Friday, February 9, 1923, Rothamsted and Agricultural Science, by Sir E. John Russell. 13 pages, illustrations, 8vo. Friday, March 9, 1923, Sunlight and Disease, by C. W. Saleeby, M.D. 6 pages, 8vo. Friday, April 20, 1923, The Growth of the Telescope, by William J. S. Lockyer, Ph.D. 13 pages, illustrations, 8vo. Friday, May 4, 1923, The Origins of the Conception of Isotopes, by Frederick Soddy, F.R.S. 13 pages, illustrations, 8vo. London, Royal Institution, 1923.

Absorption Coefficients for Homogeneous X-rays. EDWARD G. TAYLOR. (*Phys. Rev.*, Dec., 1922.)—The absorption coefficients for several organic liquids were measured for X-rays of wave-length .715 Ångstrom unit. The main question approached was this, "Is absorption of X-rays an atomic property?" Does an atom of carbon always absorb to the same extent no matter in what company it finds itself? Two pairs of isomers, pinene and limonene, $C_{10}H_{16}$, and ethyl acetate and methyl propionate, $C_4H_8O_2$, were tested. "Within the limit of the experiment the molecular absorptions are the same for the compounds of the same composition and offer additional evidence in favor of the view that X-ray absorption is an atomic property." The data calculated for hydrogen are, however, discordant and oxygen seems unwilling to fall in with the additive relation. The problem therefore must remain *sub judice* until further light comes. May it not be hoped that Lieutenant Taylor will continue to search for the solution with the same enthusiasm with which he conducted his course on X-rays at the A.E.F. University in Beaune? G. F. S.

CURRENT TOPICS.

Plant Resources for Motor Fuel.—Under this title, the *International Review of Science and Practice of Agriculture* (n. s., 1923, I, 208) collects the results of study of nine articles that have recently appeared giving data of the practicability of the manufacture of alcohol for motor purposes. H. I. Cole, chemist to the Bureau of Science, Manila, Philippine Islands, treats at length of the experiments undertaken in the Islands to ascertain the comparative economy of manufacturing alcohol from several of the raw materials there available, and reports that the Nipa palm (*Nipa fruticans Wurm.*) and blackstrap molasses offer the best and cheapest methods. Alcohol has several advantages as a motor fuel. It burns clean—without carbon deposit—the running of the engine is smoother than with the common hydrocarbon fuels, it stands high initial compression without knocking, lubrication difficulties are less, and, as far as observed, no corrosion has appeared in the valves, and no acid in the exhaust. Certain difficulties will doubtless disappear after further experience.

Mixtures of alcohol with other combustibles have given better results than alcohol alone. In South Africa, a mixture termed "natalite" (55 per cent. of rectified alcohol, 44.9 per cent. of ether, 1.11 per cent. kerosene and 0.56 per cent. of pyridin) has been successful. The percentages are doubtless by volume. Important data are given as to the cost of making alcohol in the Philippines, based upon large experience. The estimated daily cost of operating a plant producing 1000 gallons per day is \$138.29, which is about 14 cents per gallon. The figures include labor, fuel, interest, depreciation, "etc." Unless the "etc." includes the cost of the material, which does not seem likely, the actual cost per gallon will be higher than that calculated from the above total. It is not stated what strength of alcohol is produced, but presumably the calculations are made on the 95 per cent. basis. The Nipa palm is stated to be the most important and cheapest source of alcohol, as the plant grows in uncultivated places and the sap is drawn from near the ground, thus obviating the necessity of climbing. The alcoholic product of this plant has, however, been heretofore mostly employed as a beverage, and its applicability as a fuel has only recently been put to the test. The sap passes quickly into fermentation, usually arriving at the distillery with an appreciable alcohol content, though complete fermentation requires considerable time. To prevent loss by conversion into acetic acid, a mixture of the sap with molasses is usually employed. At present the palm is found extensively distributed in the Philippines and north Borneo, some 400,000 acres being estimated as covered by it.

Vegetable oils have been studied as materials for motor fuel. The investigation has been initiated on account of the danger of using the inflammable hydrocarbons in a hot climate. The ordinary vegetable oils are stated to be applicable to motors of the Diesel and semi-Diesel type. For engines of the latter type, experiments in Europe have shown that palm oil may be used as fuel without any serious modification of the engine details. The calories of vegetable oils are, of course, high. The possibility of corrosion owing to the fact that palm oil has high acidity seems to have been eliminated by the experiments.

The motor vehicle problem becomes of great importance in districts like South Africa in which the tsetse fly interferes with raising of draft animals. The possibility of using the native products for fuel will be of great advantage. The high prices for the hydrocarbon fuels with the likelihood that these will not be materially reduced in the future, constitute important reasons for experiment along the lines indicated in the article. Up to the present, investigations have centred on palm oil, but it is to be hoped that a much wider range of experiment may be soon undertaken. The substitution of such materials as alcohol or fixed oils would have the great advantage of eliminating to a large extent the fire risk that is now associated with the hydrocarbon fuels.

H. L.

Forensic Chemistry in the Punjab.—The report of Lieutenant-Colonel J. A. Black of the Royal Medical Service, on the work of the Chemical Laboratory of the Punjab, gives a vivid and interesting insight into the problems that are encountered by a chemist in a mixed population of Hindus and Mohammedans. The Punjab is a district in northwestern India stretching from the foot-hills of the Himalayas to a comparatively low land. It is watered by the Indus, of which there are five tributaries. The name is derived from a Hindu word meaning "five." Notwithstanding these rivers, the majority of the district is hot and dry, especially from April to September. The area is about 136,000 square miles, somewhat smaller than the State of Montana. The population is about 20,000,000, of which about half are Mohammedans and the greater portion of the remainder Hindus.

The characteristic of the chemical work in this laboratory is examinations in cases of poisoning. Homicidal and suicidal poisonings are extremely common. Suicides often occur from what would be considered in other countries as very trifling motives. Homicidal poisoning is occasioned by about the same class of motives that are active elsewhere. Accidental poisonings, due to ignorant use of dangerous drugs or the negligence of drug vendors, are also more frequent than in Europe and America. Arsenic is very largely used, on account of the resemblance of its symptoms to those of cholera, a disease often very prevalent in the district. Opium and Datura seeds are also frequently used, the former mostly for suicide and infanticide,

the latter for drugging food and drink, to aid in commission of robbery. An account is given of the methods of the Thugs (commonly known in English as "Thugs") who mostly use *Datura* seeds. Aconite is also used in the places in which it is found. These four poisons cover about 90 per cent. of the cases of poisoning found in the Punjab. In consequence of this limitation, the task of the toxicologist is comparatively simple. A notable difference exists between the manner in which the expert evidence is given in India and in western nations. The India chemist is comparatively rarely required to appear in court. He makes a written report, which is read. He is, therefore, not subject to cross-examination. Doctor Black inclines to favor this method, though he acknowledges that it is not without defects. As a matter of fact, it is a highly objectionable method, but it has been adopted largely because of the great extent of the district over which the expert's duties extend. Crime is greater in proportion to the population than in more highly civilized countries—at least, detected crime is greater—and personal attendance on trials would require a large body of chemists.

Physiologic methods of detecting poisons are necessary in many cases, and it is interesting to read the statement that the animals are treated with as much care as possible. This observation is probably meant to avoid any criticism from that numerous and influential portion of the British public opposed to animal experimentations. Blood differentiation is, of course, not infrequently required. The precipitin tests have been found satisfactory, and the application of them has led to conviction in a number of cases. A case is described in which a stain was shown to be a mixture of camel's and human blood, the former identified by the shape of the red corpuscles, materially different from ordinary mammal blood, and the latter detected by the precipitin test.

The work of the laboratory is by no means limited to the toxicology field. Food adulteration is extensive. A special and dangerous line is the examination of explosives in packages and letters. During the war, many articles of household use were seized by the authorities under the suspicion of being intended for employment against the government, so that a curious and miscellaneous collection of articles was referred to the chemist. As might be expected, illicit drugs are often found, especially cocaine. Drugs of this type, found to be of good quality, are turned over to the medical authorities. A great deal of the illicit importation of cocaine was in German hands before the war. The use had reached such extensive development that there was one time in the laboratory confiscated material, the money value of which at the ordinary bazaar rates was estimated at about \$160. A great variety of problems not connected with medical matters has also been considered in the laboratory, such as the best method of waterproofing fabrics for troops, the cause and prevention of corrosion of copper plates in boilers, the amount of barium carbonate required to

poison rats, for prevention of spread of plague, and whether a certain antiseptic preparation could be safely used in water.

The government has recently improved the laboratory very much, having spent about \$50,000 in new buildings and equipment. Dust is very much of an annoyance, and it is intended to sink a well for the express purpose of aiding in the development of lawns and the raising of trees so as to overcome this annoyance and also to beautify the grounds. The laboratory was located at Lahore, about sixty years ago, primarily to deal with the criminal incidents among the native population. Cases of poisoning are by no means limited to human beings. Domestic animals are often victims. A peculiar method of animal poisoning is often noted. Seeds of *Abrus precatorius* are pounded and made into a paste with water. The paste is shaped into a narrow, pointed, needle-like form, which when dry becomes very hard. It is fitted into a small cavity in a bamboo stick, which serves as a handle, pushed under the skin of the animal and the handle removed. An intense local inflammation is soon set up, which results in the death of the animal in a few days if the wound is not detected in time and the mass removed.

H. L.

Total Reflection of X-rays. A. H. COMPTON. (*Phil. Mag.*, June, 1923.)—While “direct attempts to measure the index of refraction of different substances of X-rays have hitherto failed,” yet certain features of the effects produced upon the rays by crystals have indicated that they are refracted when they enter the material of the crystal. Duane and Patterson have found a difference between the wave-length of the tungsten line obtained from the first order spectrum and that got from the second order, when calcite is used. This leads to the conclusion, derived on grounds of theory, that for the type of X-ray used the index of refraction for calcite is 8×10^{-6} less than unity. From another point of attack, the Drude-Lorentz theory of dispersion, utilizing what is known of the number of electrons per unit of volume, the frequency of vibration, etc., gives just about the same index of refraction as the other method. This agreement furnishes good presumptive evidence that refraction really exists. If refraction does take place and if, further, the index of refraction of X-rays entering calcite from air is less than unity, then we have a case of refraction analogous to that occurring when a ray of ordinary light passes from water into air. This being so, total reflection should exist. Does it exist? A narrow beam of X-rays fell upon a crown glass mirror at a large angle of incidence, or a small glancing angle. The reflected ray let into a chamber and the resulting ionization was measured. A study of the reflected radiation showed that the reflection was not diffuse but specular in character, though not perfectly regular. Now, if total reflection really takes place, the energy of the reflected ray should equal that of the incident ray. Measurement proved the energy of the former to equal 91 per cent. of that of the

latter. It may therefore be concluded that something closely approaching regular, total reflection occurs at the surface of the glass mirror. One method of determining the index of refraction of ordinary light for a substance is by measuring the angle at which total reflection first shows itself. The author now proceeds to apply this method to X-rays. For glass the critical glancing angle (90° the angle of total reflection) is $10'$, for lacquer $11'$ and for silver $22.5'$. The wave-length of the X-rays used was 1.279 Ångstrom units. The indices of refraction are calculated from the relation, index equal cosine of the critical glancing angle. All three indices are less than unity and by these quantities: Glass, 4.2×10^{-6} ; lacquer, 5.1×10^{-6} and silver, 21.5×10^{-6} . All these values agree quite well with the values computed from the Drude-Lorentz formula, which connects the index of refraction with the number of electrons per unit volume of the medium and the frequency of the radiation. It is quite advantageous to have the validity of this relation established. From it can be calculated the index of refraction of substances containing only lighter atoms, or the wave-length of an X-ray beam can be computed from a determination of its index of refraction, or, again, from a knowledge of the index refraction and of the wave-length it is possible to learn the number of electrons per atom which are affected by the incident rays. Professor Compton holds that the electronic numbers thus obtained are more reliable than those got by the two previously existing methods, *viz.*, scattering of alpha-rays by atomic nuclei and measurement of the intensity of scattered X-rays.

It is suggested that by total reflection a platinum mirror be used in order to select short wave-lengths from a beam of X-rays.

When X-rays were young, it seemed impossible to show that they did any of the things done by light. Gradually it is being shown that they possess all the properties of light. This paper definitely adds refraction and total reflection to the list.

G. F. S.

A Photographic Study of Sound Pulses Between Curved Walls and Sound Amplification by Horns. A. L. FOLEY. (*Phys. Rev.*, December, 1922.)—"That the sound energy falling upon the ear or other form of sound receiver may be considerably increased by placing the receiver at the small end of a conical horn is a matter of common observation." This increase in intensity is often explained by reference to the progressive concentration of the energy into smaller and smaller volumes of air as the narrow end of the tube is reached. Dayton C. Miller, on the other hand, attributes the effect to resonance "The effect of the horn is to reinforce the vibrations which enter it due to the resonance properties of the air enclosed by the horn. . . . The horn is an air resonator. . . . the response below the fundamental of the horn is very feeble."

A cylindrical sound wave was started by a linear discharge of electricity between two knobs. A very short time later a second electric

spark is produced at a position to one side of the first. The light from this casts the shadow of the sound wave expanding from the first spark upon a photographic plate. The existence of the shadow is due to the refraction of the light while passing through the condensation of the wave. If a series of light sparks is produced at brief intervals, the successive shadows on the plate will be circles of progressively larger radii. To study the passage of sound waves through a straight tube, a curved tube, a megaphone and a conical horn (ear trumpet) the author arranged about the axis from which the wave started four combinations of plates simulating these transmitting devices. Six photographs were taken at an average interval of .00003 second. "As would be expected, all six pictures showed that the waves passed through the straight tube and megaphone without appreciable reflection, and that the megaphone wave suffered the greater attenuation. . . . All the pictures show that there was energy reflection in every case except when the wave front was at right angles to the surface and the motion of the air parallel to the surface of the tube. In the case of the horn there was continuous reflection from one end to the other, even at the small end where the angle of the cone is very small. In the case of the crooked tube there were successive reflections. For the crooked tube show respectively an emerging and emerged wave much more attenuated in the case of the straight tube of the same size. A considerable portion of the wave energy appears to be trapped inside the tube. However, it will be observed that the reflected waves in general were headed toward the outer part of the tube. This is not true, however, of the horn. Here the advancing wave shows unmistakable evidence of intensity increase or condensation, and that it emerged from the small end of the horn considerably amplified. But most of the energy was lost as far as the small end of the horn is concerned. The lost energy was contained in the reflected waves which, as the photographs show, headed the wrong way—'backing out' of the horn."

Intensity measurements of the condensing power of a horn were made both by a Rayleigh disc and by a Webster phonometer. When the area of the large end of the horn was 256 times that of the small end, the intensity at the small end was only about 9 times as great as at the large end.

The author concludes that the "condenser" theory of a conical horn receiver is not tenable and that the amplification of sound at the small end is due both to resonance and to condensation. "Sound pulses do not 'glide about bends' in tubes and 'slip' along slanting walls 'without appreciable reflection.'" "Much of the energy of a wave entering the large end of a conical horn is reflected and eventually leaves the horn at the end it entered. The wider the horn the greater the per cent. of energy thus lost."

It is hoped that Professor Foley will find time to solve the vexed problem of the whispering gallery by the powerful experimental method that he has perfected.

G. F. S.

The K.D.B. Process of Color Photography. (*Rev. d'Optique*, Jan., 1923.)—When a corrected lens is giving an image of an object, a part of the lens can be covered up without interfering with the production of the image by the uncovered portions. Similarly different zones of the objective can be covered with selective color filters and each will continue to produce its independent image. Let three monochromatic filters, red, green and blue, be placed in the plane of the diaphragm in the form of bands side by side. Then the image on the ground glass will appear unchanged because the light traversing each filter will produce its own image and the three superimposed colored images will reproduce the natural color of the object. Now at the focus let there be placed a tiny lens of necessarily very short focus. This will project on the ground glass, a little beyond it, an image of the three bands of the filter. This image constitutes that part of the general image of the object contributed by the light impinging on the lens.

As an object to be photographed let us take a red point and for the glass plate let us substitute a sensitive panchromatic film. The red light from the point will pass through the red filter but not through the green or blue ones. The lens will project on the film no light from these two filters, but it will form a small red image of the red filter and the portion of the film under this will be blackened, while the adjacent parts corresponding to the missing blue and green images will be unaffected. The positive will be clear under the red image and black under the positions of the two other colors, as well as over the rest of the plate. Next for projection put the positive in the former position of the ground glass plate and illuminate it by white light. Only through the transparent part corresponding to the red image can the light pass. This transmitted white light will be directed by the optical system to the red part of the color filter, will emerge as red and will form a red image of the point on a screen outside of the objective. If the original point were yellow, then light from it would get through the red and the green screens and images of these parts of the screen would form on the plate. Upon reversal of the direction of the light for projection, white light would get through the positions on the positive of the red and green images. These two parts of the filter would receive this light and would transmit red and green light, respectively, and on the screen the superposition of the red and the green images will reproduce the yellow point.

In this process the sensitive layer is supported by a transparent solid whose surface on the side away from the film consists of a multitude of tiny convex surfaces acting as lenses. Each of these functions as does the single lens above discussed. On the film behind each of these, if a white object be photographed, there forms a tiny image of the color screens. The diameter of these lenses must not exceed .04 mm. A die with 520 lenses per sq. mm. was made by hand and from this the gelatin film was moulded into the requisite hillocky form.

As advantages it is claimed that but a single image is necessary for photography in colors, that the same film permits projection in black and white or in colors, that the simplicity of the process makes it accessible to all, that commercial photographic and projection apparatus can be employed, including moving picture apparatus. To use existing apparatus it is necessary only to put in the plane of diaphragm the three color screens, and to employ K.D.B. films.

K.D.B. appears to be the result of combining the initials of Messrs. Berthon and Keller-Dorian, the inventors. G. F. S.

The Spectrum of the Aurora Borealis and the Upper Layers of the Atmosphere. L. VEGARD. (*Comptes Rendus*, April 3, 1923.)—In the Geophysical Institute at Tromsø a systematic investigation of the spectrum of the aurora borealis was conducted during the summer of 1922. Thirty-three lines and two bands were found, nearly all of which can be attributed to nitrogen. There are, however, four lines which cannot be ascribed to nitrogen, hydrogen, helium or oxygen. Their wave-lengths in Ångström units are 3208.3, 3432.7, 4182.5 and 5578.4, the green ray. No trace of lines due to hydrogen or to helium was obtained even after very long exposure. Mixtures of nitrogen and hydrogen and again of nitrogen and helium were made luminous by cathode rays in the laboratory. A comparison of the light then emitted with the spectrum of the aurora led to the conclusion that "the pressure of atmospheric nitrogen at a height from 100 to 120 km. is greater than the pressure of hydrogen and of helium. At these altitudes such a layer of hydrogen and of helium as has been generally believed in cannot exist."

Some spectrograms were taken of the upper edge of an aurora while others were obtained from the lower edge of the same aurora. The green ray, whether from the upper or the lower edge, bore the same relation to the nitrogen bands found. This shows that the gas emitting this ray must have the same molecular weight as nitrogen, else a change of elevation of from 40 to 60 km. would cause a difference in relative intensity. The author therefore attributes the green ray to nitrogen and for good measure concedes to it also the three other unclaimed lines.

There remains still this to be explained. How can the light of the aurora come sometimes from a height of 500 or 600 km.? "The best supposition is a strong ionization of the upper layers by X and gamma rays from the sun. . . . The effect of the electric charge on the distribution of pressure will be similar to that of a diminution of molecular weight. Moreover the heavy electric charge on the nitrogen in the upper regions furnishes an explanation of how this element emits in the aurora lines not hitherto observed in the laboratory. The ionization so far attained in the laboratory has been insufficient."

G. F. S.

The Periodic Opacity of Certain Colloids in Progressively Increasing Concentrations of Electrolytes. J. HOLKER. (*Proc. Royal Soc.*, A719.)—The colloid chiefly studied was the emulsoid human serum, which had been previously inactivated by heating. To the serum was added a solution of sodium chloride and the opacity of the resulting liquid was measured. "With low concentrations of saline from 0 to 0.96 per cent. the opacity of the serum became less and less until it reached a minimum. Beyond 0.96 per cent. saline it increased steadily to a maximum at 2.24 per cent. and so on." No less than eleven oscillations were observed, the final maximum being attained with 24 per cent. of added sodium chloride as the net percentage concentration. As more and more of the saline solution was added the maxima and the minima both occurred at higher degrees of opacity.

The color of the light employed in testing the opacity was varied and new curves connecting opacity and concentration were plotted. "While the general level of the curves and the amplitude of the periods varied with the color of the incident light, the length of the corresponding periods was remarkably constant. These experiments, therefore, suggest that the periodic opacity of serum in progressively increasing concentrations of sodium chloride cannot be due to interference phenomena, since in the latter case the length of the periods would have varied with the colour of the incident light." The concentration of the serum also was varied. "The periodic character of the curve persisted to a high degree of dilution of the serum, and both the amplitude of the oscillations and their number increase with the concentration of the serum." Lastly a series of determinations was made at different temperatures. "At the temperatures of 20°, 30°, 40° and 56° C. the periodic phenomenon was well marked, and the amplitude of the periods increased with the temperature, so that at 56° C. it was very pronounced. On the other hand, the length of the corresponding periods remained the same for all the temperatures." At temperatures still higher irregularities manifested themselves.

When calcium chloride was substituted for sodium chloride quite marked differences in the results came to light. The initial effect of the addition of the calcium solution was to increase the opacity while the wave-lengths as well as the amplitudes of the calcium curves are different from the corresponding quantities in the sodium curves. All the neutral salts examined caused the periodic change in opacity. With HCl the periodic character of the curve was completely lost. With NaOH traces of the periodicity remained. G. F. S.

THERE are alloys possessing considerable thermo-electric powers that are too brittle to be made into wire. R. HASE (*Z. f. Phys.*, vol. 15, No. 1) shows how to utilize such substances for thermo-elements.

G. F. S.

What Limits the Ultra-violet Spectrum of Sunlight? J. DUCLAUX and P. JEANTET. (*Jour. de Physique et le Radium*, March, 1923.)—The limit of the solar spectrum toward the short wave-lengths is at about 2900 Ångstrom units. Fabry and Buisson have demonstrated that this is due to ozone in the high atmosphere. No great quantity of this gas is requisite to cut off the spectrum at the point stated, and to keep from traversing the atmosphere any radiation between the wave-lengths 2900 and 2100 Å. However, the absorption band of ozone stops at 2100 Å. Why, then, is there not found in the solar spectrum at the earth's surface wave-lengths shorter than this? Perhaps these short waves are absent when the sunlight reaches the confines of our atmosphere. This is improbable, because the light emitted by the sun is much like that coming from a black body at 6000° C., and such a body radiates a measurable quantity of energy at wave-lengths shorter than 2000 Å. Furthermore, the formation of ozone in the outer parts of the atmosphere argues for the presence there of short wave-lengths. Experiment convinces the authors that a layer of ozone lets light through of wave-lengths from 2100 to 1850 Å. This substance is thus excluded as the cause as are also CO₂, water vapor, hydrogen and the rare gases, some for lack of adequate quantity and others for lack of proper absorption. Oxygen and nitrogen would be worth investigating thoroughly did not ammonia gas by itself furnish a reasonable solution of the difficulty. From observations made on the absorption exerted by this gas the authors conclude that all radiation shorter than 2020 Å. would be extinguished by a layer of .5 mm. ammonia gas at 760 mm. pressure, on the assumption that no other gas has any part in such absorption. This quantity of ammonia uniformly distributed throughout the atmosphere would amount to .047 mg. per cubic metre of air. Measurements on the ammonia content of the air range from 0 to .092 mg. per cubic metre. G. F. S.

The Minimum Audible Intensity of Sound. C. M. SWAN. (*Proc. Am. Acad. Arts and Sci.*, 58-12.)—From the time of the first quantitative determination of this up to the present there has been no lack of interest in the subject, but the results have been discordant. In 1922 two determinations for the same pitch were published and one was more than four times as large as the other. Some measurements were based on the law of inverse squares where the law could not possibly hold, others were interfered with by wind or by the presence of birds. In many cases no account was taken of the reflection of surfaces.

In the present investigation recourse is had to the large body of experience collected in connection with the work of Sabine at Harvard. A vibrating circular diaphragm closes a hole of the same shape in the door of a room within which the observer is stationed. A formula is derived connecting the energy per square centimetre per

second that just produces an audible effect with other measurable quantities, one of which is a measure of the time of decay of the sound within the room. The observer was placed in a box so that his clothing would not absorb the sound. A series of reflectors were shifted about to eliminate the effect of the formation of acoustical interference patterns. Two persons were used in turn to take the time required for the sound to die away. The higher the pitch the more divergent became the results obtained from their observations. For a vibration frequency of 121 they differ in minimum audible intensity by only 4 per cent., while for 1021 one is twice as much as the other. Moreover, the differences are not uniformly in the same direction. The mean values are as follows: For frequency of 121, 5.7×10^{-5} ergs are needed per second per square centimetre to produce the sensation of sound. For 246, 2.7×10^{-5} ; for 493, 3.6×10^{-9} ; for 1021, 9.0×10^{-10} ergs. These results in general lie between those of Fletcher and Hegel on the one hand and the final work of Wien on the other.

G. F. S.

Compositions and Properties of the Commercial Arsenates.—

Immense amounts of arsenic compounds are used in spraying plants for protection against insects and fungi. In 1920 over 11,000 tons of arsenous oxide were produced in the United States, more than half of which was used in the manufacture of insecticides. The principal compounds used for such purposes are arsenates, those containing lead, zinc, calcium and magnesium being the most important. An elaborate study of the composition and properties of the commercial forms has been made by F. C. Cook of the Bureau of Chemistry and N. E. McIndoo of the Bureau of Entomology. The results appear in Bulletin 1147 of the Department of Agriculture. The investigation included experiments on feeding larva with materials impregnated with arsenic. Considerable difference was found in the susceptibility of different species. The maximum amount of arsenic (As) required to kill a honeybee is 0.0005 mg., but the toxic dose for a full-grown silkworm is 0.0273 mg. It is to be noted, however, that the honeybee, confined in cases, retains the whole of the arsenic compound taken, whereas the silkworm expels most of it. Lead arsenate is one of the most used compounds. The common form, PbHAsO_4 , is well standardized and stable. The commercial calcium arsenate contains more calcium than is required for a strictly tribasic salt. A sample of copper barium arsenate, made in the laboratory, was found to have strong insecticide properties.

H. L.

Atomic Weight of Gallium.—THEODORE W. RICHARDS and WILLIAM M. CRAIG, of Harvard University (*Jour. Amer. Chem. Soc.*, 1923, xlv, 1155-1167), have determined the atomic weight of gallium by the analysis of gallium chloride, and have obtained the value 69.716.

J. S. H.

Work in 1922 of the Department of Terrestrial Magnetism, Carnegie Institution, L. A. Bauer, Director. Any citizen of the United States who is conversant with the fine scientific work conducted under the direction of Doctor Bauer cannot fail to experience great satisfaction that our country is continuing to make this important contribution to the solution of the problems of terrestrial magnetism.

The *Carnegie*, the non-magnetic oceanic observatory, reached Washington in November, 1921, and is now ingloriously berthed at a wharf. This vessel has a total of 253,320 miles to its credit and observations so numerous as almost to need the integral calculus for their summation. When the department first began its work on the seas errors in declination were disclosed amounting to even as much as 16° . "Errors in inclination not infrequently amounted to over 10° and the values of the earth's magnetic intensity were found erroneous at times by amounts reaching and even exceeding 10 per cent." In spite of the long voyages of this vessel and of its predecessor, the *Galilee*, it is still stated that there are from 500,000 to 1,000,000 square miles of ocean area where no recent accurate magnetic observations have been made. The outstanding need for the future, however, seems to be a study of the variations of terrestrial magnetic elements with time. It is rather discouraging to learn that the United States Coast and Geodetic Survey reports that the rate of change of the direction of the compass "has varied so much recently that values carried forward from 1915 are in some cases not dependable."

While the observers were not on duty on the *Carnegie* they were employed in various quarters of the globe. The list of places where the department carried out observations in 1922 is an astounding one—Egypt, Tunisia, Sinai Peninsula, Singapore, Canton, Asia Minor, Syria, Islands of Eastern Mediterranean, Arabia, Siberia, Western Australia, New South Wales, New Zealand, Greece, Constantinople, Miami (Fla.), Venezuela, Brazil, Argentine, West Indies, Bahamas, the Solomon Islands and New Guinea, and several countries of Europe. Mr. Coleman used a copra-trading schooner to reach the Marquesas and the Tuamotu Islands in the Pacific.

A conference for planning future work was held in January, 1922. Among the recommendations made were the following, that magnetic and electrical observations be made in the upper levels of the atmosphere, that "because of the unsatisfactory distribution of magnetic observatories in the Southern Hemisphere, the complete program of work in terrestrial magnetism, atmospheric electricity, earth-currents and allied observations at the two magnetic observatories (Watheroo, Western Australia, and Huancayo, Peru) be fully carried out," that laboratory investigations be conducted on such subjects as the development of instruments, experimental reproduction of observed cosmic and magnetic phenomena and general magnetism and that theoretical studies be made of the results of previous analyses,

of line-integrals and of "possible bearings on the properties and constitution of matter." As typical of the kind of experimental work done in the laboratory may be cited the establishment by S. J. Barnett of the fact that a piece of iron when rotated becomes a magnet. "Rotating any ferromagnetic substance investigated at one revolution per second is equivalent to placing it in an axial magnetic field with intensity -3.5×10^{-7} gauss, within about one part in ten."

Here is one field of physics that abounds in adventure in its observational side and who can predict what a flood of light will come with the finding of the cause of the magnetism of the earth?

G. F. S.

Distillation of Water for Municipal Supply.—In the course of a communication on the water supply of the Antofagasta Railway, Robert M. Fox, Chief Engineer of the Waterworks of Delagoa Bay, refers to several phases of construction that are of importance in practice. The Antofagasta Railway links the interior of Bolivia with the Pacific coast. It was originally constructed to connect certain nitrate deposits with the port, and was a narrow gage line about twenty-two miles long. It now has a total length of over 1200 miles and crosses the mountains at an elevation of about 13,000 feet. The region in which the nitrate earth (caliche) is found is about thirty-four miles wide, extending along the coast for sixty-six miles. It is entirely rainless. The scarcity of water occupied the attention of railway authorities as soon as the extension of the track began. Even in the extension to La Paz only one river is crossed (twice) and one of its tributaries. At the beginning of operations the company depended on water distilled from sea water at the coast. Pipe lines were afterwards extended to more suitable supplies than that afforded by a river—San Pedro—which had a high degree of hardness, and the following sources are now in operation:

San Pedro River	10,712 feet above sea level
Palpana springs	11,000 feet above sea level
Polapi springs	12,486 feet above sea level
Siloli stream	14,154 feet above sea level

The last three sources are potable. The San Pedro water is not used for drinking or boilers, but for the lixiviation of the caliche. The details of construction and operation of the pipe lines and other accessories of this supply system are given in the paper, published in the *S. Afr. Jour. Sci.* (1922, xix, 120). One point deserves special notice. The company fearing that a breakdown of the pipe line supply might occur, by which a large population would be without water, set up two sextuple sets of multiple distilling apparatus with a capacity of 44,000 gallons (presumably Imperial gallons of 10 pounds) per day. These have been operated at what seems a high fuel

efficiency, a ratio of thirty pounds of water per pound of coal having been obtained. Welsh coal (approaching anthracite) has given the best result. Briquetted fuel and Australian coal have less heating power. Proper comparison, however, cannot be made without statement of the analysis of the respective samples. Oil has been substituted in a multiple distilling apparatus set up at a seaport about forty-five miles from Antofagasta, which has been in satisfactory operation for seven years. The ratio of oil burnt to water obtained has been 1 to 36. Moreover, although the cost of oil is nearly the same as that of coal, only two men are required for the oil furnaces while eight are needed for serving the coal. H. L.

ON February 27, 1923, the British Science Guild held a meeting in the Mansion House, London, in order to direct attention to the claims of research and progress in science to be matters of national import. Sir J. J. Thomson emphasized the need of methods of bringing scientific matters to the attention of large masses of the population so that legislative enactments for the benefit of science could receive public support. The neglect of men of science "was vigorously pressed by Sir Ronald Ross. It might be supposed that the discoverer of the cause of cancer or tuberculosis would soon become a millionaire, but he pointed out that Sir David Bruce, who solved the problem of sleeping sickness, was now in Madeira unemployed, and there were three or four others whom he could name. He suggested that the nation should pension scientific discoverers of preëminent worth, and allow them to go on working as they pleased."

It may be a wholesome, though a disagreeable, discipline for us Americans to demand of ourselves an answer to the question, "Which would receive the greater recognition among us, an actor in a new, popular film, or the man who should find a means of reducing tuberculosis to the comparative insignificance of smallpox?" G. F. S.

Conversion of Methyl Chloride into Methanol. RALPH H. MCKEE and STEPHEN P. BURKE, of Columbia University (*Ind. Eng. Chem.*, 1923, xv, 682-688), have studied the conversion of methyl chloride into methanol (methyl alcohol). This conversion is not produced by steam at a temperature of 350° C., even in the presence of silica, zirconium dioxide, anhydrous aluminium chloride or anhydrous calcium chloride. Aluminium hydroxide is not suitable as a catalyst since it dissociates into the oxide and water. Calcium hydroxide is an excellent catalyst; with the exception of a small amount of methane and hydrogen, the methyl chloride is practically quantitatively converted into methanol and methyl ether; less than 0.1 per cent. of the methyl chloride is converted into formaldehyde. A slight deposition of carbon on the catalyst occurs; at a temperature of 350° C., the catalyst becomes gray, at 450° C. black; as the concentration of water vapor in the gaseous mixture is increased, the deposition of carbon is noticeably decreased. J. S. H.

The Heat of Vaporization of Neon. E. MATHIAS, C. A. CROMMELIN and H. KAMERLINGH ONNES. (*Comptes Rendus*, April 3, 1923.)—Using data determined in the cryogenic laboratory of the University of Leyden, where recently a temperature only a fraction of a degree above the absolute zero has been attained, the authors have calculated the value of L , the heat of vaporization at the critical temperature, for the monatomic gas neon. In the table T represents the critical temperature.

Gas.	T Absolute Degrees.	L Calories.
Oxygen	154.29	50.06
Argon	150.65	38.10
Nitrogen	125.96	47.9
Neon	44.38	20.8
Hydrogen	33.18	106.5

G. F. S.

"I SHOULD like to emphasize that there has seldom, if ever, been such an interesting period in the history of physical science as the present time. It was a great shock to the scientist to find that the velocity of light was independent of the motion of the observer. Some explained it by saying that the earth dragged the ether along with it, but this is contradicted by the phenomenon of the aberration of light. Fitzgerald and Lorentz suggested independently the contraction hypothesis which gives a rational explanation, but which is very difficult to verify by experiment. The relativity theory does not explain the nature of the phenomenon, but it indicates that the hypothesis of the ether is not a necessity. So many exciting problems have arisen in recent years that Rutherford's experiments showing the transmutation of gases have not received the attention they deserve. These experiments mark a new epoch in the history of science, and in the future they may have marvellous commercial developments. The further our knowledge of physical science extends the more closely does it affect us in our normal everyday mental and physical life. A country that neglects the study of physical science cannot take a leading place among civilized nations." (From the presidential address of Dr. Alexander Russell to the Physical Society of London, Oct. 27, 1922.)



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ENGINEERING PROBLEMS SOLVED BY PHOTO-ELASTIC METHODS.*

BY

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TWO LECTURES DELIVERED AT THE ROYAL INSTITUTION OF
GREAT BRITAIN, MAY 17 AND 24, 1923.

LECTURE I.

(a) IMPROVEMENTS IN APPARATUS.

(b) CONTACT PRESSURES AND STRESSES.

IN some former lectures which I had the honor to give at The Royal Institution in 1912, a brief survey was attempted of the application of polarized light to engineering problems of stress distribution, and incidentally a few essential facts were described which are necessary for grappling with problems of stress distribution by this form of experimental investigation. It will, therefore, not be necessary on this occasion to devote time to these considerations and it seems more appropriate to describe one or more fields of investigation which have been pursued during the intervening years, and it is this course which it is proposed to follow here.

Everyone who has carried out experimental work is well aware that, in general, a great deal of time must be devoted to devising and constructing new apparatus or improving existing forms in order to attack problems which have not been attempted before, or if attempted are only partially solved, and it frequently happens

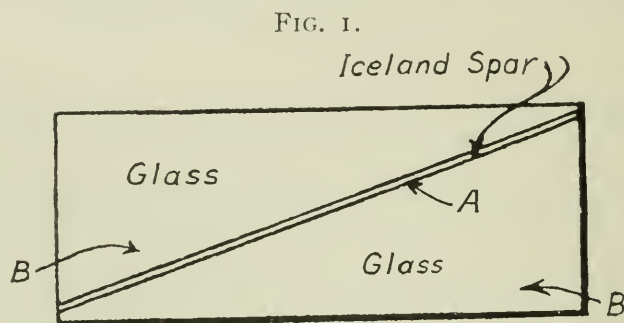
* Communicated by Prof. E. G. Coker, Associate Editor of this JOURNAL.

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that much more time is spent in this way than the investigation itself ultimately takes. The design and construction of measuring instruments of precision is in fact a branch of experimental research, which is nearly always a prominent feature in any physical investigation, and especially so in engineering science. It will not, therefore, be a waste of time to give an account of some useful improvements in apparatus which have been devised for photo-elastic research during the last few years.

Polarized Light.—A fundamental requirement in this subject is a beam of plane or circularly polarized light of sufficient purity and intensity to reveal the state of stress in loaded models of a machine or structural element constructed from a transparent



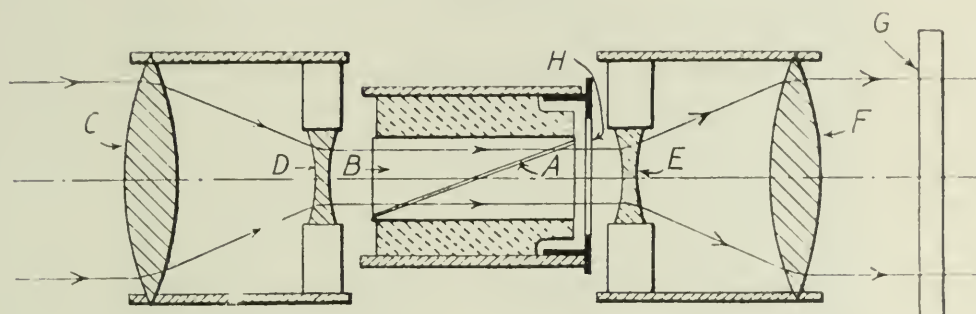
Polarizing prism.

material. An Iceland spar prism cut in the manner invented by Nicol, or in other modified ways devised since, is by far the most perfect means of obtaining the kind of light required. Even the best alternatives, so far as I am aware, are much inferior in polarizing effect, but the scarcity of suitable spar is so great that suitable large prisms constructed wholly of this rare mineral are rarely obtainable, and much ingenuity has been devoted to overcoming this difficulty. Among the many which have been suggested, one may be mentioned which appears to be especially valuable, since it reduces the amount of spar to a minimum. It is in fact found that a very thin plate of spar *A* (Fig. 1) suitably cut in relation to the crystallographic axes and mounted between glass wedges *B* is almost, if not quite, as efficient a polarizing medium as the all-spar prism devised by Nicol and the numerous variants of it suggested since. It is even possible to build up such a plate from small elements cut and mounted in precisely the same manner so as to form a larger plate little if any inferior to a single one cut from a much larger crystal.

One of the great difficulties in this kind of work appears therefore to be solved, but so far only small prisms appear to have been constructed in this way, and the beam of light from it has to be enlarged by the addition of lenses which serve to contract the somewhat large beam to a suitable size to pass through this polarizing prism and afterwards to expand it to a suitable size on emergence.

A simple way of carrying this out, devised by Mr. A. L. Kimball and myself, is shown in Fig. 2 in which a beam of ordinary light passes through a double convex lens *C* and the cone of rays formed in this manner is rendered parallel by a double concave lens *D* to pass through the polarizer. The beam

FIG. 2.



Arrangement of polarizer and analyzer.

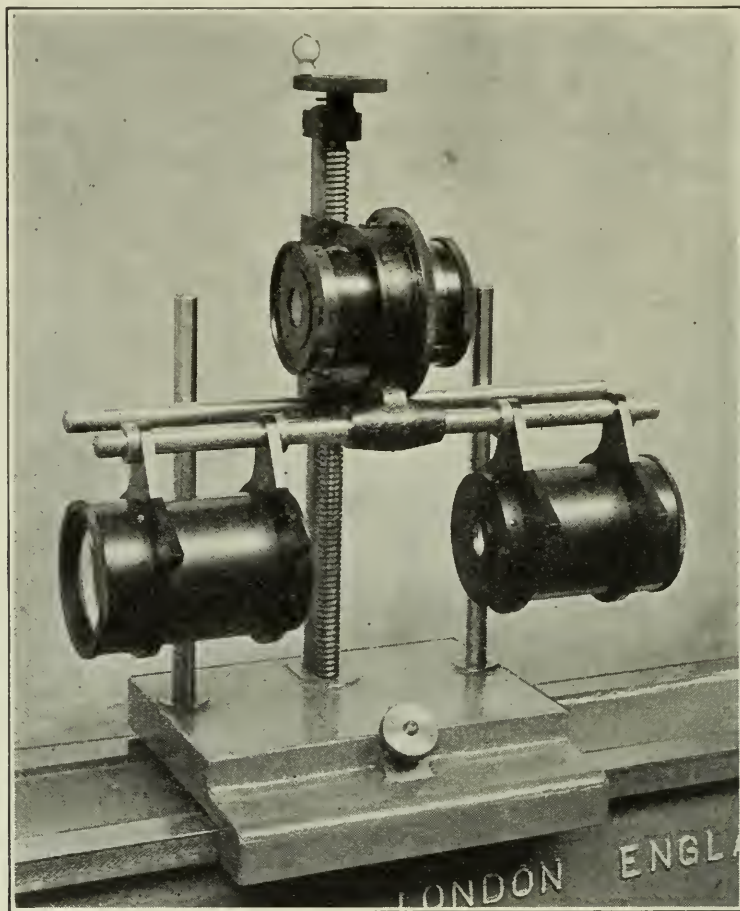
is afterwards expanded by an inverse arrangement of lenses *E*, *F* to the required size for observing the condition of the transparent model *G*.

The interposition of a quarter-wave plate of mica *H* may be used to convert this plane polarized beam into a circularly polarized beam when required.

The form which this arrangement has taken in the most recent designs is shown in the accompanying photograph of a polarizer (Fig. 3), with the cases containing the lenses for obtaining a conical beam turned down in order to show the arrangement of the central prism and quarter-wave plate more clearly. In use, however, these lenses are set correctly with respect to the optical axis, as shown in the second photograph (Fig. 4). Both central prism and quarter-wave plate are mounted in suitable casings, so that each can be turned round through any angle quite independently of the other, and set by cylindrical scales indicated in the photograph. Each part can be readily removed when the

lens systems are turned over as described above. The frame carrying this prism and the lens system is also capable of adjustment vertically by a screw, and a horizontal adjustment for bringing the optical axis in line with other lenses is secured by a screw which pulls the base casting into contact with the ver-

FIG. 3.

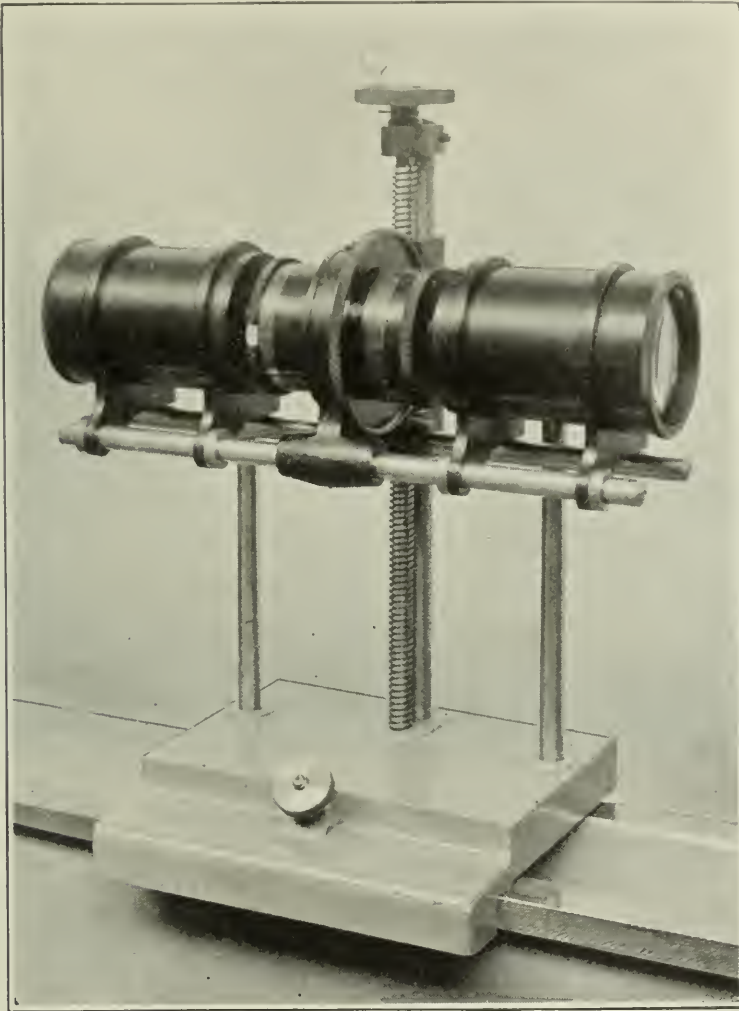


Polarizing prism with the converging and diverging lens systems lowered.

tical face of a lathe bed on which all the required pieces are mounted. Although there are some interesting kinematic details in this arrangement, it will not be necessary to describe these here, as they are clearly shown in the photograph. In general the polarizing prism requires to be set in position in relation to several other optical and mechanical devices, and usually so that the stress effects in the model under examination can be compared with those observed in a loaded tension member by projecting both

on to a screen or else photographing one or both on a color plate. The most convenient way is, therefore, to provide such an arrangement of lenses that both model and tension member can set in separate parallel fields and be projected clearly on to the same plane. A method of doing this, suggested to me by Pro-

FIG. 4.



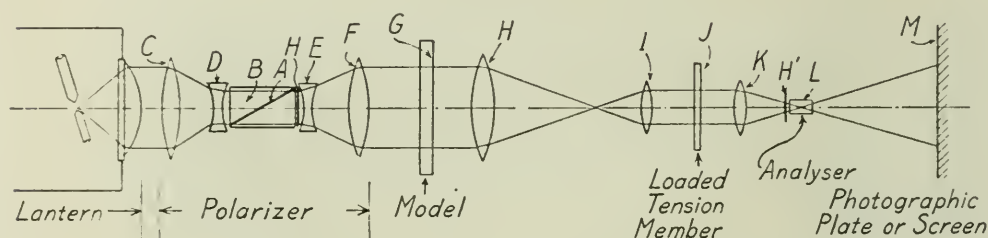
Polarizing prism mounted and ready for use.

fessor Filon, is shown in Fig. 5, in which the parallel beam emerging from the polarizer passes through the model *G* and is then reduced in size by a lens *H* and later brought to parallelism by a second lens *I* to allow observations on the comparator bar *J*. After passing through this the beam is brought to a conical pencil by a lens *K* in order to pass through the quarter-wave plate *H'* and analyzer *L* and is finally received either on the screen *M*,

or else a photographic plate if permanent records are required. This optical scheme gives all the flexibility required for experiment and gives a much better result than any scheme in which both objects have to be set in the same parallel field, since in such an arrangement it is usually difficult to get clear images of both bodies and one is necessarily somewhat out of focus.

A complete installation of this type is shown in the accompanying photograph (Fig. 6), representing an apparatus designed for workshop and laboratory use, in which all the parts described with reference to Fig. 5 now appear, with the exception of the model and the comparator bar. As will be observed, each piece is adjustably secured by a suitable grip to a vertical standard,

FIG. 5.



General arrangement of photo-elastic apparatus.

while the horizontal adjusting screws of the bases serve to grip each member to the bed, and also to give each part the requisite horizontal adjustment. In addition the bases are so constructed that they can be used on an ordinary table, so as to facilitate the assembly of the apparatus in relation to testing machines and models of large size.

Lateral Extensometer.—At a Friday evening Discourse¹ in 1916, methods of measuring the stress effects observed in a transparent model were described by comparing them with those observed in a simple tension or compression member cut from the same material and loaded in such a manner that the stress t_1 in it just balances the principal stress components p and q at a point in the model. We have in all such cases

$$t_1 = p - q$$

but this measurement is not in general sufficient, as we usually desire to know p and q separately. This further knowledge can also be obtained by purely optical means² or, if preferred, by

¹ Appendix (21).

² Appendix (18).

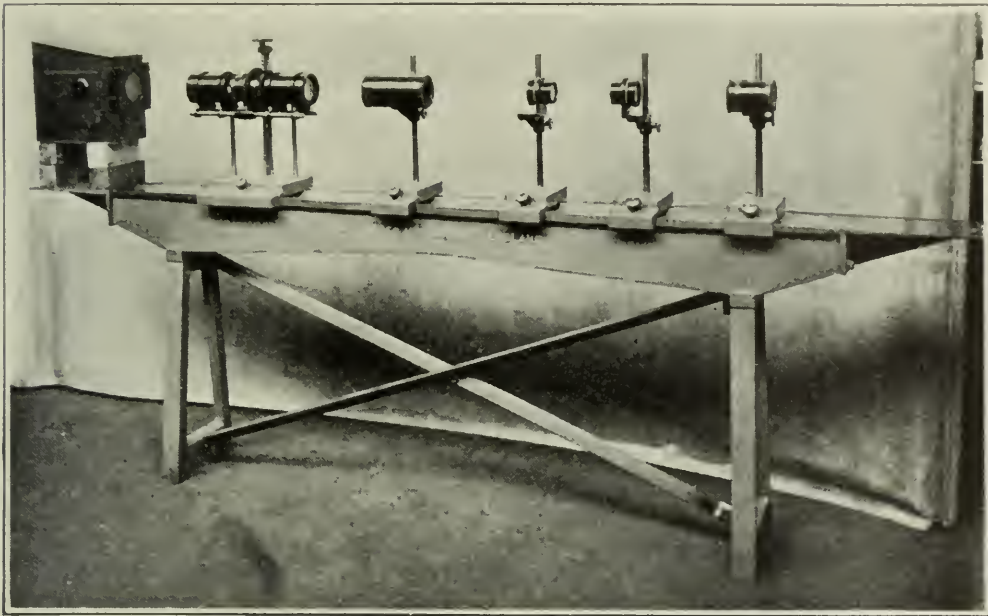
measuring the change in the thickness at the same point and comparing it with the lateral changes in a simple member under tension or compression. For equality we have

$$t_2 = p + q$$

and this relation is easily found.

An instrument for measuring these lateral changes was described at the time, itself an improvement on earlier models, but a great many minor features have been added since which

FIG. 6.

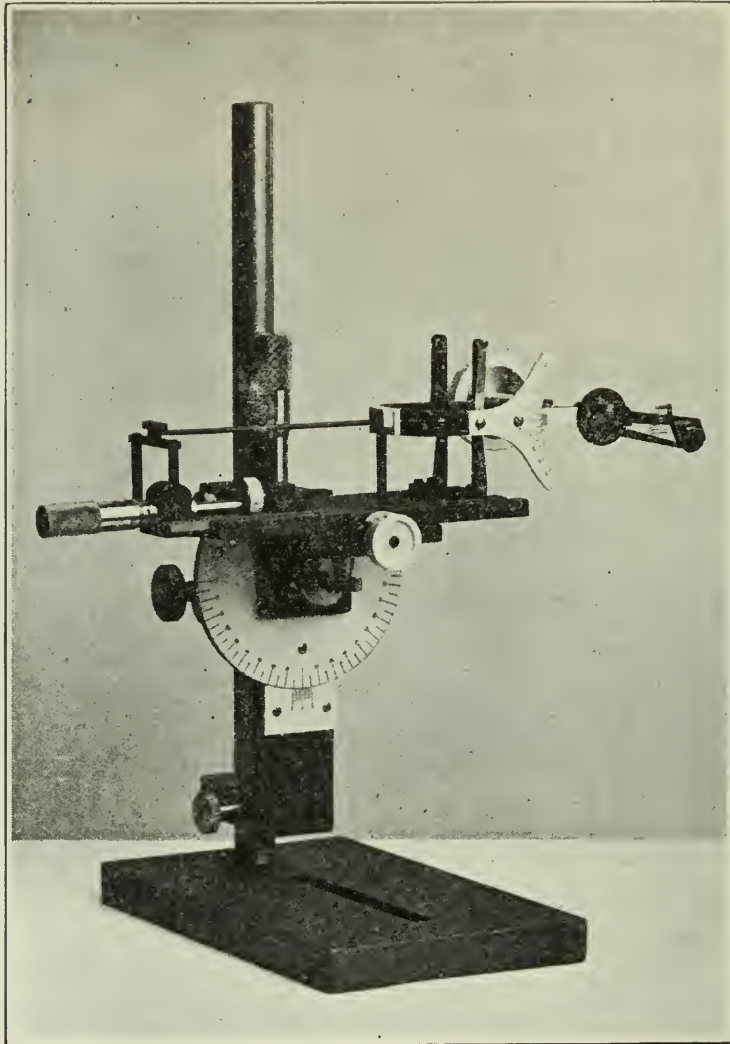


Apparatus for photo-elastic experiments designed for use in engineering workshops and laboratories.

have largely increased its usefulness, and as now made it is the somewhat complicated looking instrument shown in Fig. 7. It is, however, much easier to manipulate than the earlier forms. It will be readily understood that one must have the means of setting the lateral extensometer so that the measuring needles can be brought to any place on the model, and to effect this the supporting framing is now mounted to slide on the single vertical pillar shown, under the control of a micrometer screw which appears immediately in front of the pillar, and which bears against a second block also itself capable of sliding on the same pillar, but usually fixed thereto by a friction grip. In some cases it may be desirable to move the instrument vertically a slight amount

without touching the micrometer screw, and to effect this a second micrometer screw of small pitch is interposed, in series with the micrometer screw, which can be turned round to effect slight adjustments. This enables an operator to start a set of

FIG. 7.



Lateral extensometer.

observations in a given plane with the vertical micrometer at an initial zero reading, an obvious advantage.

The arrangement is in fact equivalent to having two micrometers in line, only one of which is used for measurement. In addition provision is made for the introduction of end measure standard blocks, so that the range of the micrometer can be

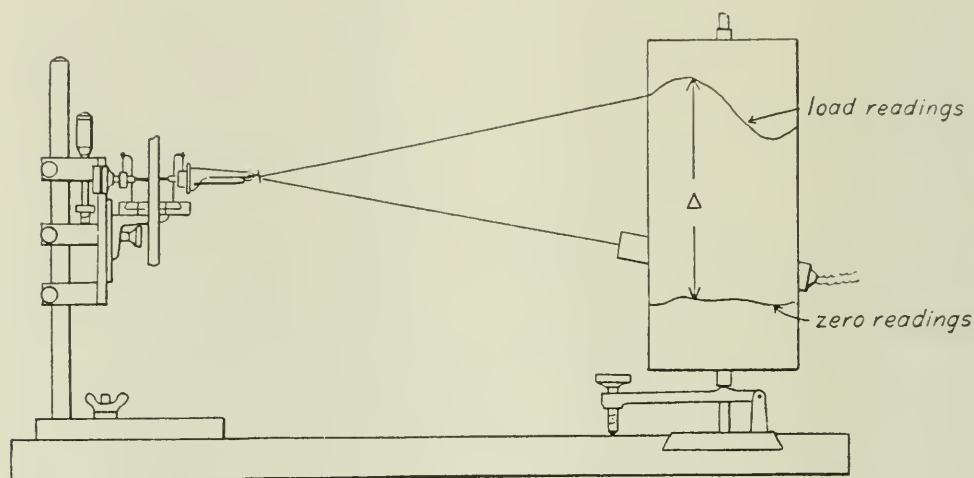
extended from say one inch to several inches. Finally the central reference block forms one element of a simple sliding pair with the main frame, and this latter can therefore be secured in such a position that a vertical plane through the main pillar has any required azimuthal angle. This arrangement dispenses with a second pillar used in earlier forms. The main cross slide carrying the extensometer has somewhat similar arrangements, but in addition it is itself mounted on a transverse slide controlled by a micrometer screw, seen in the foreground, so that a slight adjustment can be given to bring the extensometer into such a position that the axis of its tail-rod is in the central plane of the main slide.

As will be observed, the horse-shoe frame of the extensometer is supported by a three-point suspension consisting of two fine wires at the front ends and a spherical ball bearing on the end of the tail-rod. This allows a certain amount of freedom to swing, which it is found desirable to have, but carries with it the possibility that the measuring needles may not be exactly perpendicular to the sides of the model. This is, however, ensured by the cross-slide screw mentioned above, and also by two fine lines, one on the extensometer and another on the main cross slide, which lie end-on to one another when the setting is correctly made. It sometimes happens that a line along which measurements are desired is neither horizontal nor vertical, and it is convenient, therefore, to mount the main cross slide on a horizontal axis so that it can be set to any desired inclination by a graduated circle and vernier plate on the main vertical slide. This inclined arrangement causes the spot of light reflected from the mirror of the extensometer to move at an angle to the vertical. This is inconvenient for reasons which will appear immediately. In order to so arrange the instrument that the spot of light shall always move in a vertical plane, the casing containing the multiplying gear of the extensometer is arranged to turn round the axis of the contact needles and it is set at the required angle by a graduated scale and vernier plate mounted on the horse-shoe frame of the extensometer, as shown on the right-hand side of the photograph. This latter scale and the one attached to the main cross slide are both graduated so that when both are in correct adjustment the readings are the same.

With these arrangements the lateral changes at points a few thousandths of an inch apart can be measured with comparative

ease, and in fact it was soon found that the principal difficulty lay in the fact that the time required to analyze several hundred such observations in a laboratory notebook was excessive, and the more so that at least two different observations are required at each point because the parallel surfaces touched by the needles are never flats in the optical sense; they are usually in such a condition that the natural variation of thickness from one point to another is of the same order as the changes produced by stress. In order therefore to get an orderly arrangement so that measure-

FIG. 8.



Arrangement of lateral extensometer and drum recorder.

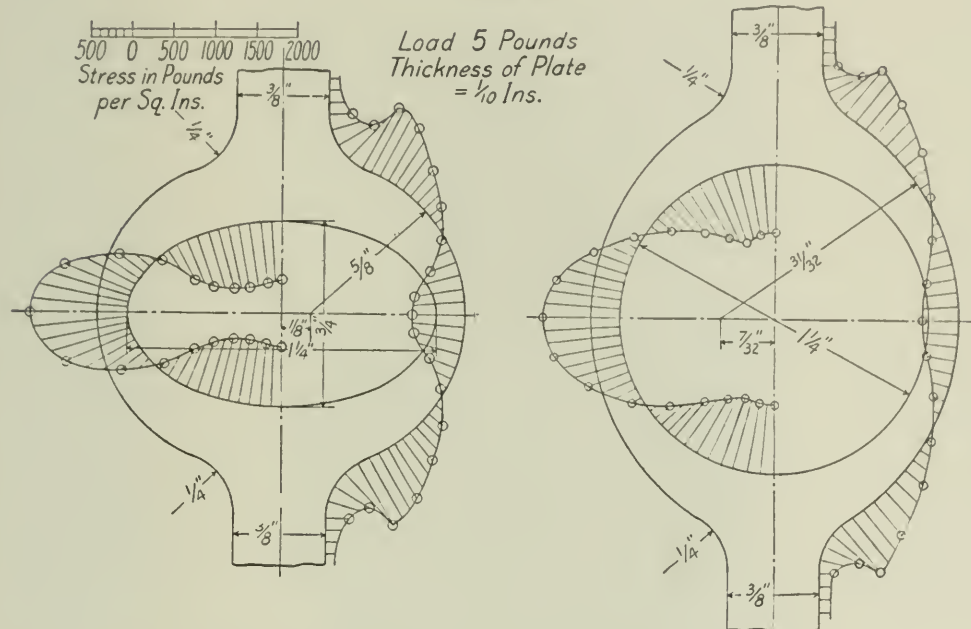
ments of each and every observer could be readily analyzed, the plan was adopted of plotting each observation directly on a large sheet of squared paper wrapped round a cylindrical barrel (Fig. 8) pivoted on a vertical axis. The movement of the spot of light due to the natural variation of thickness along any line of the specimen is taken as a base line from which the observations of the change due to stress can be measured and the corrections required for angularity of the beam of light and the like can be drawn in with paper templates. The final results are thus obtained without any arithmetical calculations and are usually all on the same sheet. As a matter of detail it may be interesting to mention that it is found convenient to reduce the stress measurements so that they refer to a standard thickness of material whereby two independent investigations by different observers can be compared.

As will be noticed in the photograph, the drum of the recorder

can be raised or lowered to bring the zero reading of the extensometer to a definite position on the paper, and when a large model is under examination it is mounted on a transverse slide and is moved by hand to follow the horizontal movement of the extensometer.

The arrangement could obviously be easily made autographic by a mechanical gear connecting the rotating drum and the

FIG. 9.



Stress distributions at the contours of ring-shaped springs.

micrometer slides and using photographic paper, but so far this has not been found necessary.

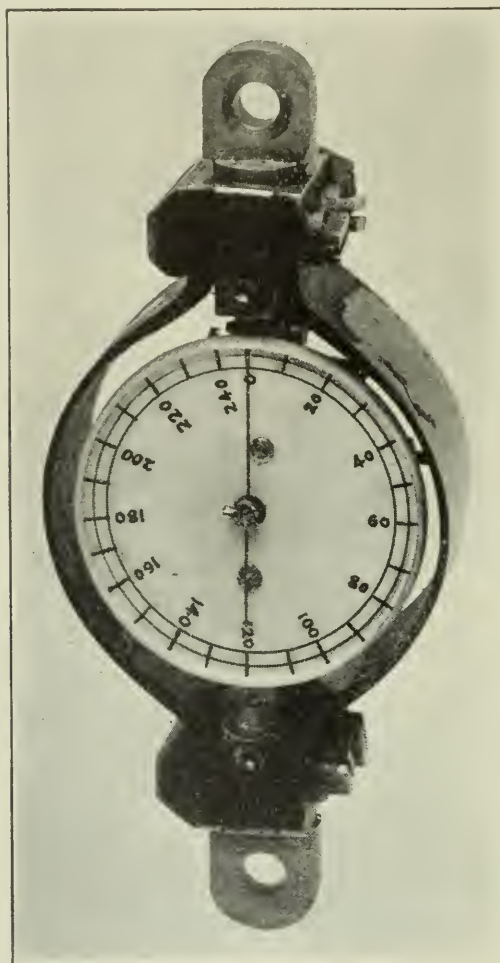
Spring Balances for Use in Experiments on Transparent Models.—A minor difficulty which often presents itself in examining the stress distribution in a model is to load it properly in a convenient and easy manner. Probably nothing is better than a dead weight if it can be used, and this is generally possible for experiment on the effects of bending, but becomes highly inconvenient and sometimes impracticable when tension, compression and shearing forces are applied, since the range of stress for which the simple optical law holds,³ is generally large and is, for example, about 3500 pounds per square inch for nitro-cellulose. The manipulation of the heavy loads required for such stress is

³ Appendix (26).

therefore usually difficult. Much can be accomplished, however, with a minute form of testing machine of a single or compound lever type, in which the load is applied by a straight pull spring balance with a very open scale suitably calibrated.

Such a case presents itself when employing a loaded tension member for comparison with the stresses observed in a model,

FIG. 10.



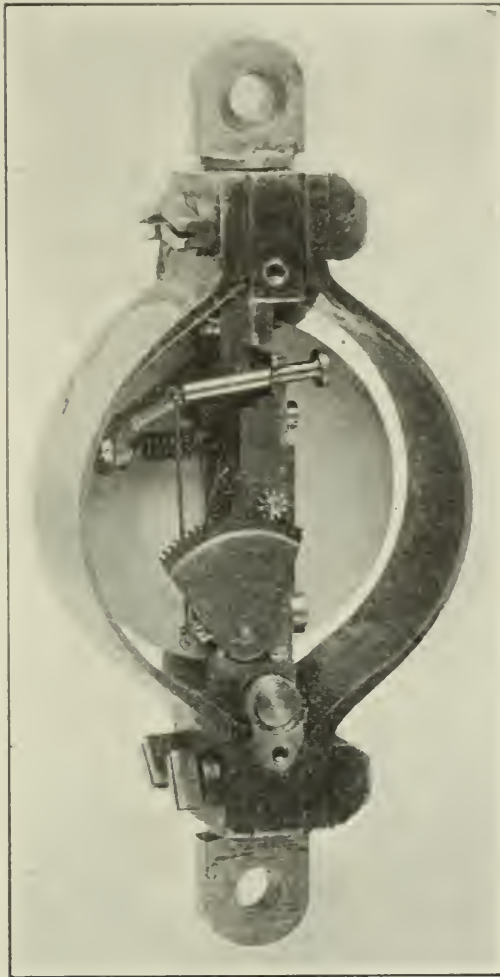
Spring balance, face view.

and a useful arrangement of this kind is a very small double lever testing machine mounted on a graduated disc and having a central hole to permit the passage of a beam of light. The disc is adjusted on a vertical rod by a suitable clamp, it has a horizontal cross slide in the base and can be turned round the optical axis of the polarized beam by aid of a fitting at the back of the

disc. With these three adjustments the tension member can be brought into any required position in the field of view.

Even this device, however, may be inconvenient for some kinds of measurement, and spring balances of very small size would often be preferable, but in general these latter are

FIG. 11.

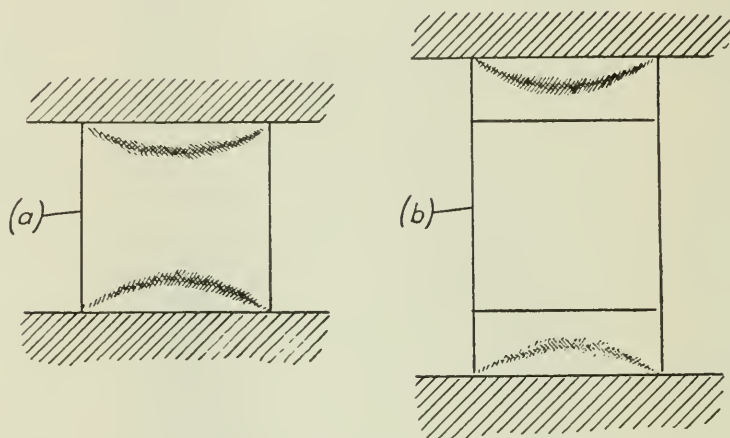


Spring balance, back view showing mechanism.

much too bulky for the average loads, required of from 200 to 500 pounds. It has, in fact, been found necessary to devise an alternative form, and the essential feature made use of is the change of form produced in a solid metal spring made preferably in a ring-shaped form in such a fashion that within the elastic limit of any part of it a sufficient change of length in some direction is produced which can be magnified to operate

a dial indicator. In order to obtain a suitable form of spring it is possible to make use of experiments on transparent models to find a shape such that the stress distribution shall not be so excessive anywhere that the limits of elasticity are over-passed. Some of the models of these springs under load are now projected on the screen by aid of a beam of polarized light, and it is possible at a glance to form a good idea of the characteristic features of the stress distribution since the minor principal stresses in most cases are not sufficiently great to affect the color

FIG. 12.



(a) Transparent block under normal load between the plates of a testing machine.
 (b) The same block when stressed by aid of intermediate blocks of the same material and of the same cross-section.

effects very much, and a simple color scale enables one to estimate the stresses produced fairly accurately. Two of the forms examined are also shown in Fig. 9 and the stresses found at their contours are indicated thereon. Having chosen in this manner the most suitable spring form it is only necessary to magnify the extension in a steel counterpart in some suitable direction, say along the line of pull or transversely to this line by a suitable mechanical device free from zero errors. After some trouble this condition has been satisfied, and several spring balances constructed in this manner and about the size of a rather large watch have been made and are found to work in a satisfactory manner. In the example shown in the photographs (Figs. 10 and 11) a spring balance is depicted having a dial of two inches' diameter and weighing four and one-quarter ounces, which measures loads up to 240 pounds. It would have been just as easy to make this

spring measure loads up to a ton or possibly in the other direction to weigh a letter, without alteration in size other than that required by the proportions of the spring itself. A further advantage of this form, other than that of mere reduction in size, is that the energy stored in the balance is so small that, should the model break, the release of this energy in the spring itself is insufficient to cause any damage to the apparatus employed, or to the balance itself due to the sudden return of the index and its attached mechanism to zero position.

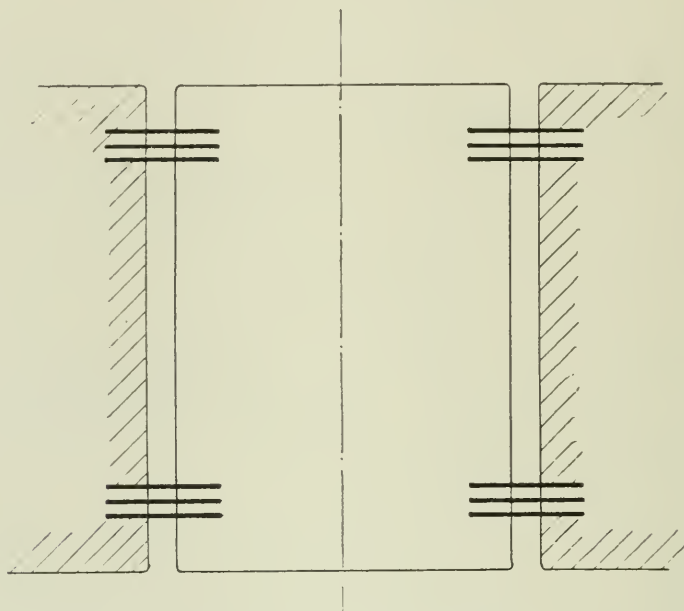
It is perhaps useful to mention in connection with the measurement of loads that the case of pure compression requires special consideration, as it is exceedingly difficult to apply correctly owing to the defective construction of most of the testing machines now in use, and also to the effects of contact pressure between materials differing in physical and dimensional properties as described in an earlier paper.⁴ In regard to the latter properties, it is found that if say a cube of material is subjected to stress between parallel pressure plates, there is, in general, a region of stress at each end due partly to the difference in physical properties of the two materials in contact, and partly to the dimensions of the surfaces, so that the central part only is in pure compression as indicated in Fig. 12. If, however, the block is pressed between plates of the same size and of the same material, as indicated in the same figure, the local disturbances only occur in the end blocks, and the central one is then under approximately pure compression stress. The mechanical difficulty of keeping the compression plates parallel, and yet so arranged that the total load applied shall be measurable, is considerable. It is most effectively solved in the well-known Emery testing machine, but for the small compression machines needed in photo-elastic investigations it is convenient to use a form of apparatus⁵ which has been in use for a number of years in my laboratory, consisting of a long cylindrical plunger (Fig. 13) secured in the main frame of the machine by thin concentric diaphragm plates at each end, so as to allow a very small displacement axially by the elastic deformations of the annular diaphragm. The load on the lower plate can be applied in any convenient fashion provided the two pressure plates are kept exactly parallel, and the applied force P at

⁴ Appendix (30).

⁵ Appendix (11).

the top plate attached to the plunger is conveniently measured by a single lever connected to the plunger by a thin spring plate and pivoted on a second spring plate in a similar manner to those used in the Emery testing machine. The use of spring plates and guiding diaphragms adjusted to unstrained positions instead of combinations of knife edges has the additional advantage that any energy stored in them by their change of shape is restored when

FIG. 13.



Plunger secured by diaphragms and having a limited movement axially.

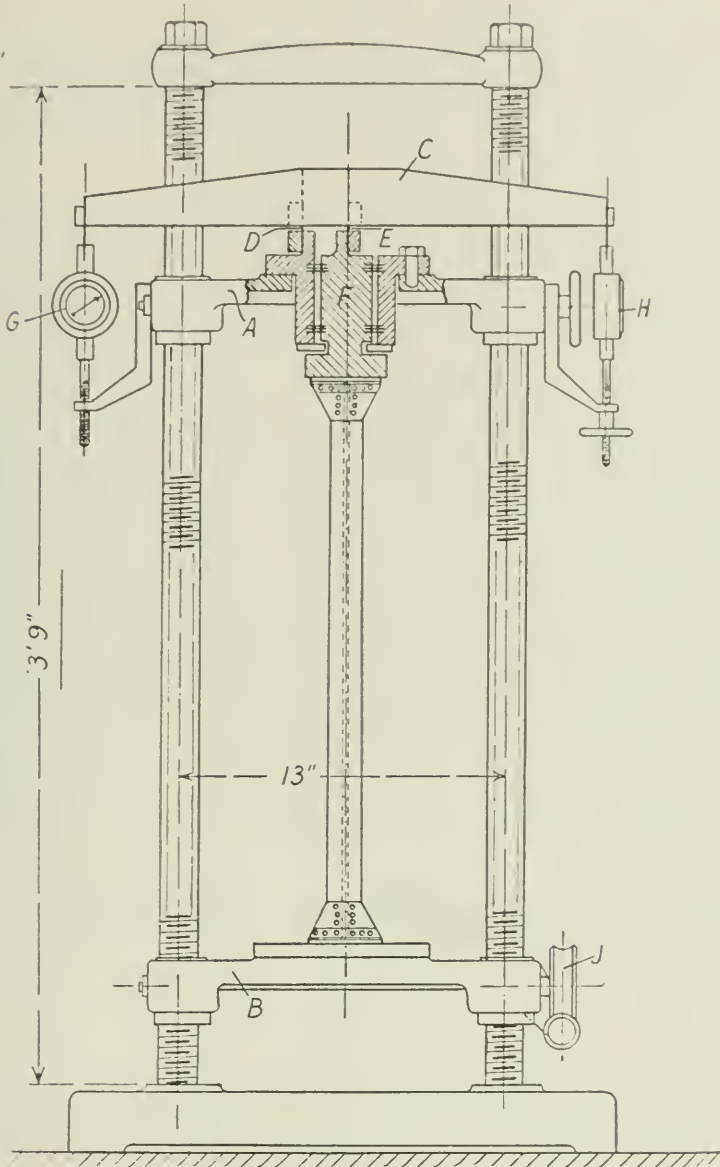
this equilibrium position is gained and is also available to help restoration, whereas any frictional effect is irreversible.

The applied force can be measured at the end of the lever by dead weights, or, if too large, by a small spring balance as indicated here. Such a machine on a larger scale is of use for models of considerable size; one of this type was constructed about two years ago for the General Electric Company of America, in which the detail features were designed in collaboration with their representative, Mr. A. L. Kimball, Mr. F. H. Withycombe and Mr. Macklow Smith. This machine was also capable of applying both tension and compression loads. In a larger testing machine now under construction at University College the same general arrangement is being used and is represented by a diagram (Fig. 14) in which it will be noted that both the upper head *A* carrying the measuring apparatus and the lower head *B*

for applying load are carried on screwed standards by nuts connected by worm-gear drives, so that each head can be traversed by gearing to any required position.

The main lever *C* for weighing the load is supported on a steel

FIG. 14.



Testing machine for large transparent models.

plate knife edge *D* so designed by photo-elastic methods that the tendency to buckle under the direct thrust upon it is reduced to a minimum, thereby removing a difficulty experienced in earlier forms. The ends of this plate are also constructed to provide ample bearing surfaces at the points of connection to the casing

and the main lever so that no slip can take place between them. The steel plate E for the plunger F is of the same form, and each end of the lever is also provided with similar steel plates to carry dead weights or, when heavy loads are necessary, spring balances G and H of the forms described above.

An experimental column is shown in position in this machine under load applied through the lower head by the worm gear J and weighed by the spring balance H , while the spring balance G is prevented from exerting any influence by the removal of the nut on the screwed extension.

The Connection between the Stress Distribution Observed in Transparent Models and Those in Actual Structures and Machines.—It is natural to enquire how far one may rely on the stresses observed in plate models constructed of transparent materials to infer the stresses in the actual element of a machine or structure, and this has been subjected to rigid scrutiny from every possible aspect. It can be shown that in general the identity is complete, but it would take too long to give the evidence here which may be found in several papers by my colleague, Professor Filon, Mesnager and myself, and which prove, if the laws of similarity are observed, that the stress systems produced in bodies of different materials are precisely the same within the limits of elasticity of each material when the body is enclosed by a single boundary, or in which the loads on separate boundaries are themselves in equilibrium. There is a theoretical reason for this, which may be found in treatises on elasticity, but is worth referring to here.

The stress strain equations for a plate loaded in its own plane are

$$\frac{\partial \widehat{xx}}{\partial x} + \frac{\partial \widehat{xy}}{\partial y} = \frac{\partial \widehat{xy}}{\partial x} + \frac{\partial \widehat{yy}}{\partial y} = 0 \quad (1)$$

leaving out as non-essential the terms involving volume forces and for these equations, and we have a solution for these stresses in terms of a function χ in the form

$$\widehat{xx} = \frac{\partial^2 \chi}{\partial y^2}, \quad \widehat{yy} = \frac{\partial^2 \chi}{\partial x^2}, \quad \widehat{xy} = -\frac{\partial^2 \chi}{\partial x \partial y} \quad (2)$$

while the strain relations are readily shown to be

$$\frac{\partial^2 \epsilon_{xx}}{\partial y^2} + \frac{\partial^2 \epsilon_{yy}}{\partial x^2} - \frac{\partial^2 \epsilon_{xy}}{\partial x \partial y} = 0 \quad (3)$$

The equations connecting the strains and stresses have the form

$$\left. \begin{aligned} mE\varepsilon_{xx} &= m\widehat{xx} - \widehat{yy} \\ mE\varepsilon_{yy} &= m\widehat{yy} - \widehat{xx} \\ mE\varepsilon_{zz} &= -(\widehat{xx} + \widehat{yy}) \\ mE\varepsilon_{xy} &= 2(m+1)\widehat{xy} \end{aligned} \right\} \quad (4)$$

and it is easily possible with these relations to express the fundamental equation of plane stress in terms of χ only in the form

$$\frac{\partial^4 \chi}{\partial x^4} + \frac{\partial^4 \chi}{\partial y^4} + 2 \frac{\partial^4 \chi}{\partial x^2 \partial y^2} = 0 \quad (5)$$

which, as will be noted, contains no elastic constants and hence the stresses which are all derived from χ cannot depend on such constants.

We have therefore, apart from experiment, conclusive evidence on theoretical grounds that experiments on transparent models do actually inform us what are the stresses in materials used by engineers. If it were possible to solve the last equation $\nabla^4 \chi = 0$ in an absolutely general fashion, we should be able to find by calculation the stress in any plate-formed body under any loading in its own plane, but it seems unlikely that such a general solution will be found, and even if it were it is more than probable that its complexity would be an insuperable bar to its use in most of the cases which occur in practice.

Although a further matter does not arise in the researches described here, I must not omit to mention, however briefly, the important question of the stress distribution in multiply-connected bodies like that of a solid connecting rod, let us say, in which the loads on the internal boundaries do not balance separately and independently of one another. In that case the fundamental stress equation is not free from elastic constants, and photo-elastic experiments require a correction to fit them for use in other cases where the material is of a different nature, but the recent researches of Filon⁶ show that, in the majority of cases, this correction is within the error of experiment, and that in any case its value may be determined by experiments.

⁶ "On Stresses in Multiply-connected Plates," Prof. Filon, F.R.S., British Association Report, 1922.

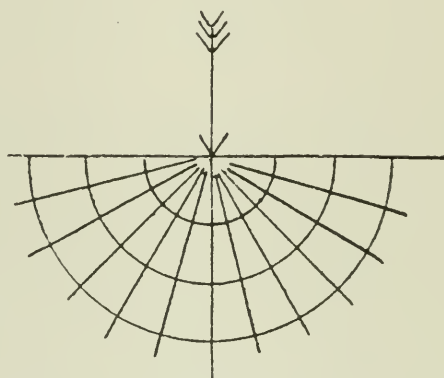
CONTACT PRESSURES AND STRESSES.

(a) *Point Contact*.—An important field of work in which photo-elastic investigation can be of considerable service is that of the distribution of contact pressures between plane and curved surfaces of which there are any number of examples of practical importance in engineering work. The simplest possible case is that in which we have a concentrated load P applied perpendicularly to the straight edge of a semi-infinite plate for which

$$\chi = \frac{P}{\pi} \widehat{r\theta} \sin \theta \quad (6)$$

is a solution of equation 5, which satisfies all the conditions of

FIG. 15.



Lines of principal stress due to normal point loading at the edge of a thin plate.

the problem, and gives a stress system found from equations (2), expressed in polar coördinates and defined by

$$\widehat{rr} = \frac{2P}{\pi} \cdot \frac{\cos \theta}{r}, \quad \widehat{\theta\theta} = \widehat{r\theta} = 0 \quad (7)$$

or the stress in the plate radiates in all directions from the point of application of the load, and diminishes linearly with the distance, and also varies with the obliquity of the direction according to a cosine law. The lines of principal stress all meet at the point of application of the load, and the corresponding orthogonal system consists of circles struck from the point of application as centre, as shown in Fig. 15, but it will be noted that these latter are lines of zero principal stress since $\widehat{\theta\theta} = 0$. Optically this stress system is represented by color bands in the form of complete circles touching the boundary at the point of application, and with centres on the line of load for here

$$p - q = \widehat{rr} - \widehat{\theta\theta} = \frac{2P}{\pi} \cdot \frac{\cos \theta}{r} = A \quad (8)$$

where the magnitude of A depends on the order of the color band. Now for any definite value A , we have for a distance R_0 immediately below the point of application

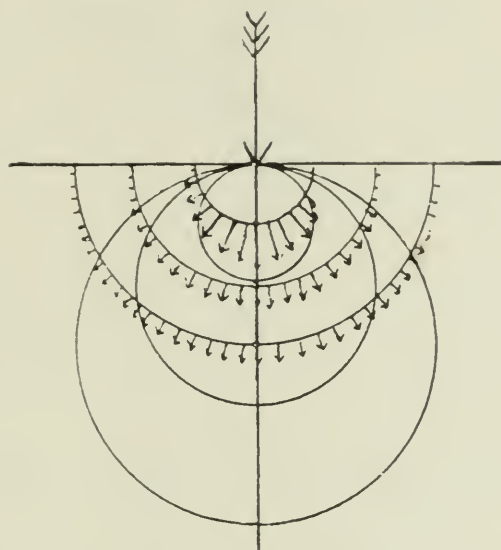
$$\frac{2P}{\pi} \cdot \frac{1}{R_0} = A$$

so that

$$r = R_0 \cdot \cos \theta. \quad (9)$$

Some of the circles corresponding to this last equation are

FIG. 16.



Stress distribution due to normal point loading at the edge of a thin plate.

shown on Fig. 16, while the stress systems across the circles of principal stress are also indicated.

This distribution was approximately verified by Carus-Wilson⁷ and has also been examined by Mesnager.⁸ It is important to note that if the concentrated load is applied at a point well inside a very extended plate, it would produce all round radial stress of the same type with two systems of color bands in the form of circles having centres along the line of loading and passing through its point of application, as indicated in Fig. 17,

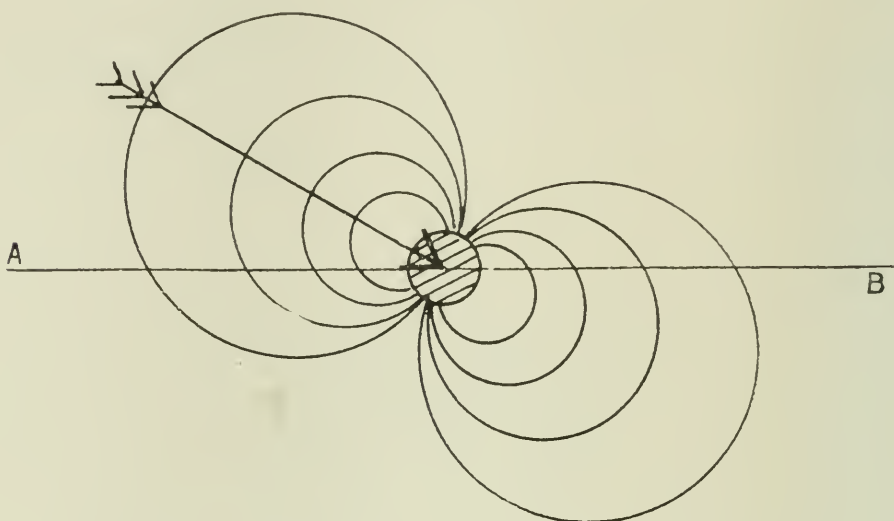
⁷ "The Influence of Surface Loading in the Flexure of Beams," Prof. C. A. Carus-Wilson, *Phil. Mag.*, Dec., 1891. See also Appendix (30).

⁸ "Utilization de la double réfraction accidentelle du Verre à l'étude des efforts intérieurs dans les solides," M. A. Mesnager, Association Internationale pour l'essai des Matériaux. VI^e. Congrès New York, 1912.

and it is possible to show this experimentally by gripping a plate of nitro-cellulose over a very small area and exerting a tangential stress upon this latter as you now see in the polariscope.

In practice, concentration of load is never quite so perfect as the simple theory assumes, and there is always a distribution over

FIG. 17.



Color band system developed by tangential stress at a point in a plate.

a finite area which, if it is uniform and of intensity p along the straight edge of a plate, can be calculated, since then

$$\chi = \frac{p}{2\pi} (r_1^2 \cdot \theta_1 - r_2^2 \cdot \theta_2) \quad (10)$$

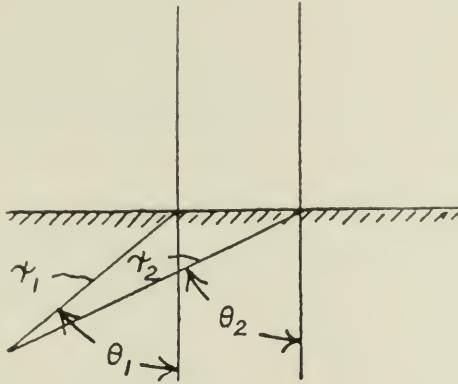
satisfies all the conditions when r_1 , θ_1 , and r_2 , θ_2 are measured from the ends of the block (Fig. 18). We then have a stress system

$$\left. \begin{aligned} \widehat{rr} &= \frac{p}{\pi} (\alpha + \sin \alpha) \\ \widehat{\theta\theta} &= \frac{p}{\pi} (\alpha - \sin \alpha) \\ \widehat{r\theta} &= 0 \end{aligned} \right\} \quad (11)$$

with reference to an origin at the edge where a vector bisecting the angle $(\theta_1 - \theta_2) = \alpha$ intersects this line. The lines of stress are therefore confocal conics with foci at the ends of the contact area of the small block as Fig. 19 shows. Even with a very large plate, however, this distribution is not obtained exactly, as it seems impossible to distribute a pressure uniformly over a small area

when it forms part of a larger one, for you will notice in the accompanying experiment in which a block one inch square is loaded at the centre of one side by a block $\frac{1}{8}$ inch wide that there is a very complicated stress system caused by non-uniform pres-

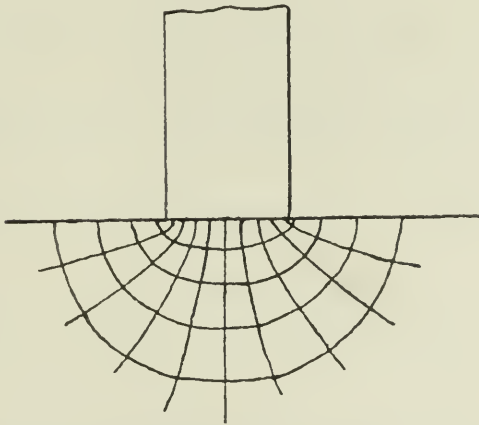
FIG. 18.



Coordinate system for a plate uniformly loaded over part of its edge.

sure at the contacting surfaces with a considerable increase of intensity at the end points. It has in fact been shown⁹ that, not only is there non-uniform pressure, but that in general the

FIG. 19.



Lines of principal stress due to normal load uniformly distributed over a small part of the edge of a large plate.

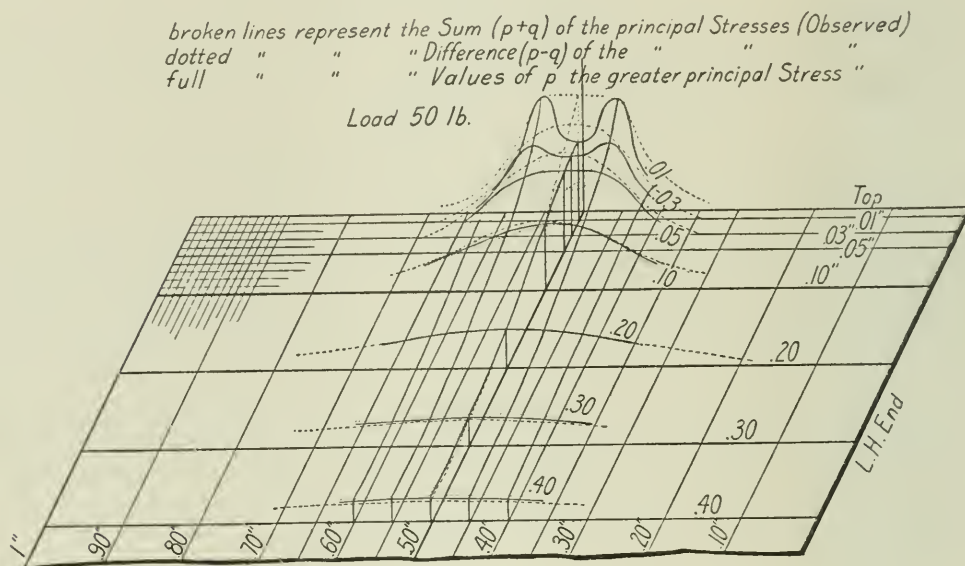
supported lower edge of a very large plate loaded above in this way is also under non-uniform contact pressure, which tends to concentrate about the line of load, while the outer ends tend to rise.

This has also been shown independently by my colleague,

⁹ Appendix (30).

Professor Filon,¹⁰ who has proved that in a block of depth b there cannot be contact at the lower edge at distances beyond $1.35 b$ from the line of a single concentrated load. It is particularly noticeable here how intense the contact pressure is at the ends of the loaded area of the upper face. The stress distribution when measured confirms this and we find, as the semi-perspective view (Fig. 20) shows, that immediately under the centre of the contact area the pressure is least and approaches to a maximum at the end points. Moreover, this type of distribution tends to maintain itself, and only gradually dies away and ultimately

FIG. 20.



Actual distribution of contact pressures and stresses in a block loaded normally over a small part of its edge.

becomes a non-uniform pressure across horizontal sections with a maximum value at the centre. As we have seen above, even if such a block is loaded over the whole of a pair of opposing faces, we do not find that it is under uniform compression stress if materials of different kinds are in contact, as they almost always are when cubes and rectangular blocks of cement stone, brick and the like are tested to destruction, and in fact it appears impossible to obtain absolutely uniform stress in such cases unless the contacting surfaces are of the same material and the same size.

¹⁰ "On the Approximate Solution for the Bending of a Beam of Rectangular Cross-section under Any System of Load." L. N. G. Filon, *Trans. Royal Soc., Series A*, Vol. 207.

When we turn to cases of contact stress of curved surfaces, there is a bewildering variety of practical problems which deserve our attention, but I will only refer briefly to one of these, the contact pressures of the teeth of gear wheels, which you now see in action in the polariscope.

You cannot fail to notice that the pressures of these curved surfaces produce systems of color bands of the line contact type, somewhat modified by the curved contours from those of an earlier case, and in addition there are intense stresses caused by the bending action of the applied forces, which latter produce dangerous stresses at the roots of the teeth. Attention was called to this in an early paper ¹¹ and some experiments ¹² made by my former research assistant, Dr. Chakko, now Professor of Engineering in the University of Madras, show, in the case of a solid spur wheel, the lines of principal stress in the tooth, one example of which is shown in the upper part of Fig. 21. The stress system is a somewhat complicated case of contact stress owing to the form of the curved boundary, at which, as the color bands indicate, the stress attains maximum values. The stress distribution over the boundary of this tooth for this position is shown in the lower part of Fig. 21, and its variation along it indicates how intense is the contact stress and also how very unlikely it is for the usual methods of calculating the stresses in teeth to be correct. More recently stress distributions in electric railway motor pinions ¹³ have been determined by similar methods. Some further case of contact pressures and stresses produced in piston rings and chain links ¹⁴ have also been examined in my laboratory.

LECTURE II.

(a) THE TESTING OF MATERIALS IN TENSION.

(b) THE ACTION OF CUTTING TOOLS.

Some very interesting cases of stress distribution occur in the testing of materials, and it is proposed in the first instance to briefly refer to the chief features of interest which have been

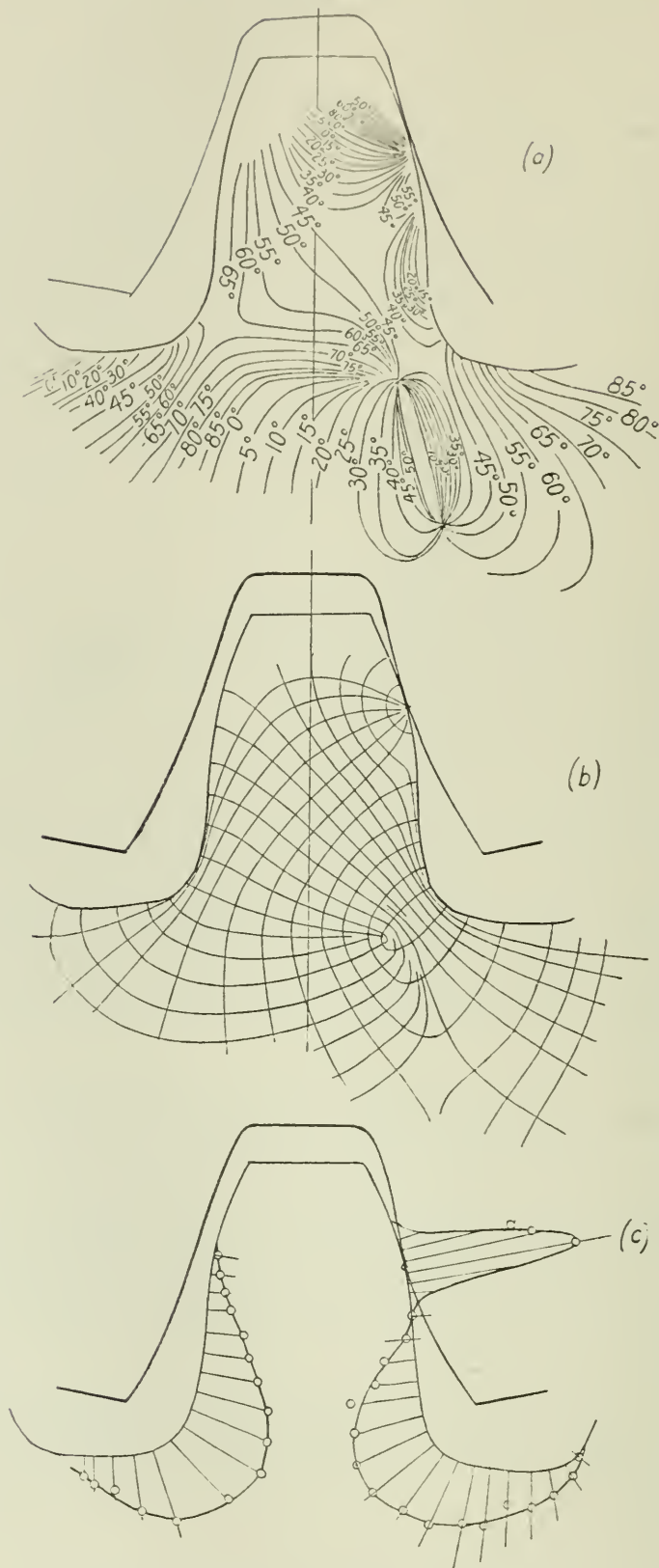
¹¹ Appendix (4) and (20).

¹² Appendix (36).

¹³ "Stress Distribution in Electric Railway Motor Pinions as Determined by the Photo-elastic Method." P. Heymans and A. L. Kimball, *Am. Soc. Mech. Engrs.*, Dec., 1922.

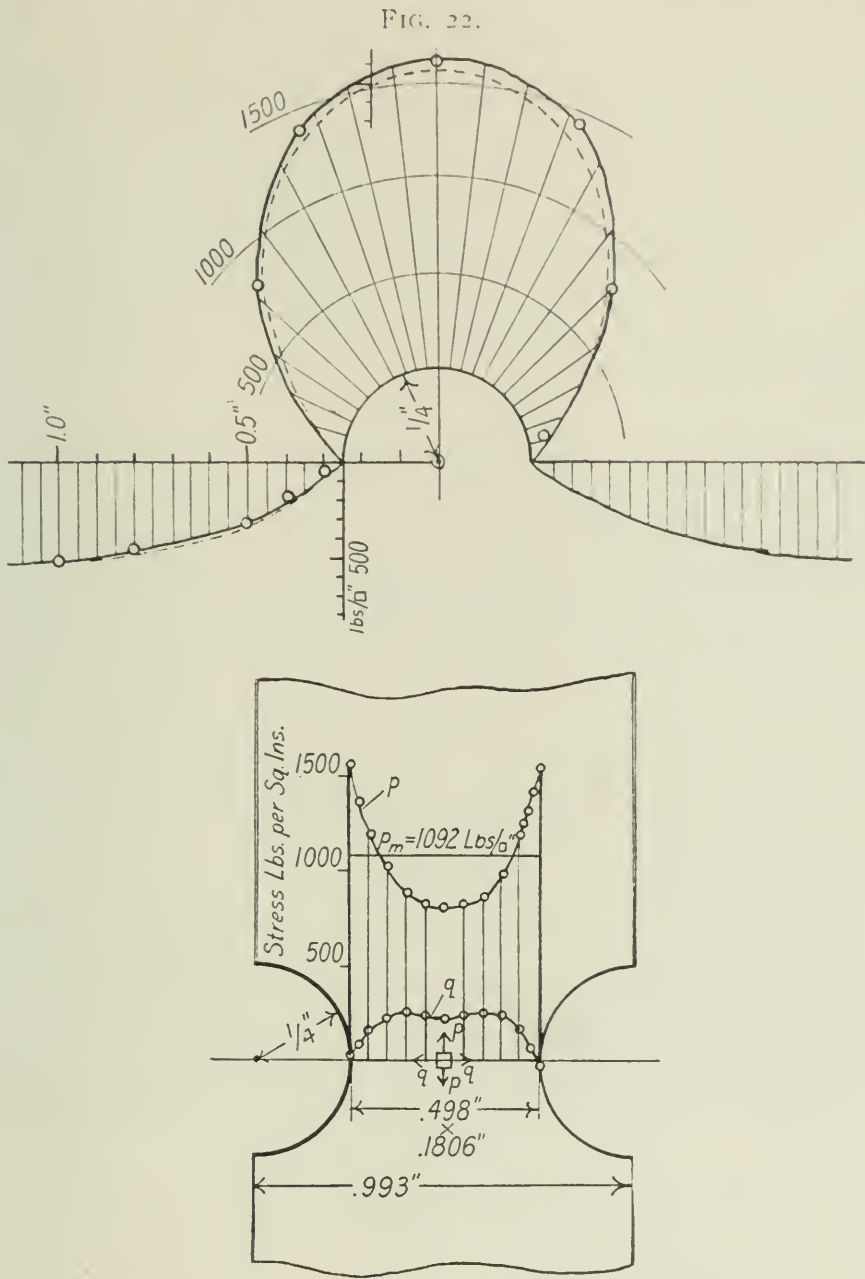
¹⁴ Appendix (35).

FIG. 21.



(a) Isoclinics. (b) Lines of principal stress. (c) The contour stresses of a tooth of a cog-wheel.

found in some recent investigations¹⁵ on this subject. It will be convenient to start with a primitive form of test piece from which others may be derived, and for this purpose a simple strip



Stress distribution in a tension member with symmetrically placed semi-circular notches.

is selected—four units wide having two symmetrically disposed semi-circular notches in it of one unit radius. As you observe when this is loaded in the polariscope, the color picture produced

¹⁵ Appendix (24).

indicates a rather complicated stress system, which extends well into the parallel end portions of the member. At the minimum section there is clearly a very uneven distribution of stress, and measurements of the principal stresses p and q indicate that the axially directed stress varies in the manner shown in Fig. 22 with a maximum at the contours about 92 per cent. greater than the stress at the centre. In addition there is a cross stress q which is zero at the contours, rises to a maximum very rapidly as we proceed towards the axial line and then falls slightly in value towards the centre. Around the semi-circular contours the uneven distribution is still more marked as the extreme points of the semi-circles are not under any stress for any load within the elastic limit of the material.

Such a form is obviously entirely unsuitable for a tension test piece, although it has occasionally been so used, and a more practicable form is obtained when a central parallel strip is introduced of say two units in width, now shown under stress in the polariscope, in which as will be observed there is a non-uniform color distribution which invades this central parallel portion, so that we may be sure that only a part of this latter is under pure axial tension.

It is also to be remarked that the colors observed at the contours indicate that the stress is an absolute maximum near the joint of the quadrantal arcs with the straight central part, and a complete exploration of the whole area shows that this is a correct inference. A number of specimens have been examined which have precisely similar ends, but central parts of different lengths, and measurements have shown that so long as these latter parts are of adequate length, the distribution of stress in the ends is always the same within the elastic limit, and that the zero isoclinic lines form the boundaries of the region of complex stress. It is therefore possible to determine for any test specimen of plate form how much of its central length is in pure tension and to assign a limit of length at which the central portion ceases to be in pure tension.

The effective length in tension for any given contour can be easily determined for any given case, and in Fig. 23 four cases are shown which have been worked out in this way. In these the larger breadth B of the specimen is 0.9316 inch, the smaller breadth b is 0.4600 inch, and the variable factor is the radius

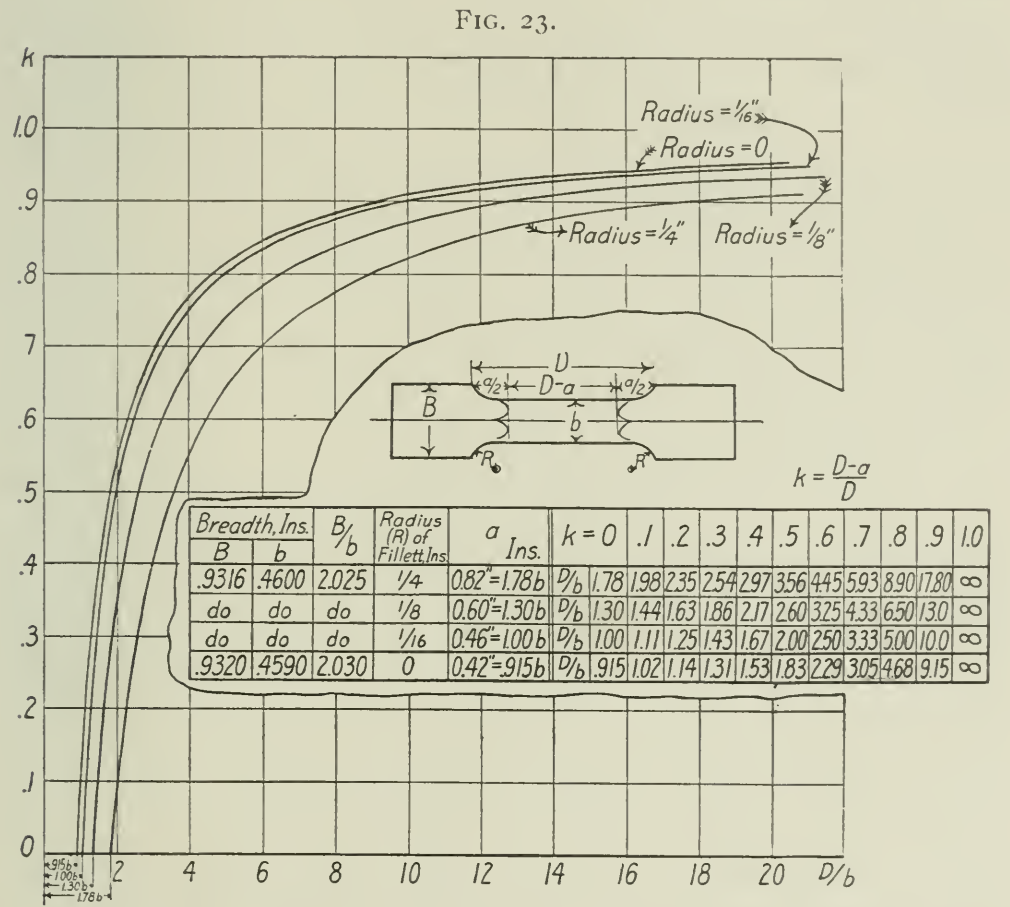
of the fillet joining the ends, as marked in the figure. It will be noticed here that the smaller the radius the greater is the length in pure tension, but this is accompanied by proportionately higher

TABLE I.

Tension Specimen of Rectangular Cross-section 0.4600 in. by 0.1812 in. under a Uniform Stress of 1180 pounds per square inch with Enlarged Ends 0.9316 in. wide.

Radius of connecting curve (in.)	1/4	1/8	1/16
Maximum stress in pounds per sq. in.	1480	1725	1890
Percentage increase of stress.	23.4	43.8	57.8

stress at the fillet, as is shown in Table I, from which it appears that the maximum stress at the fillet is always appreciably larger

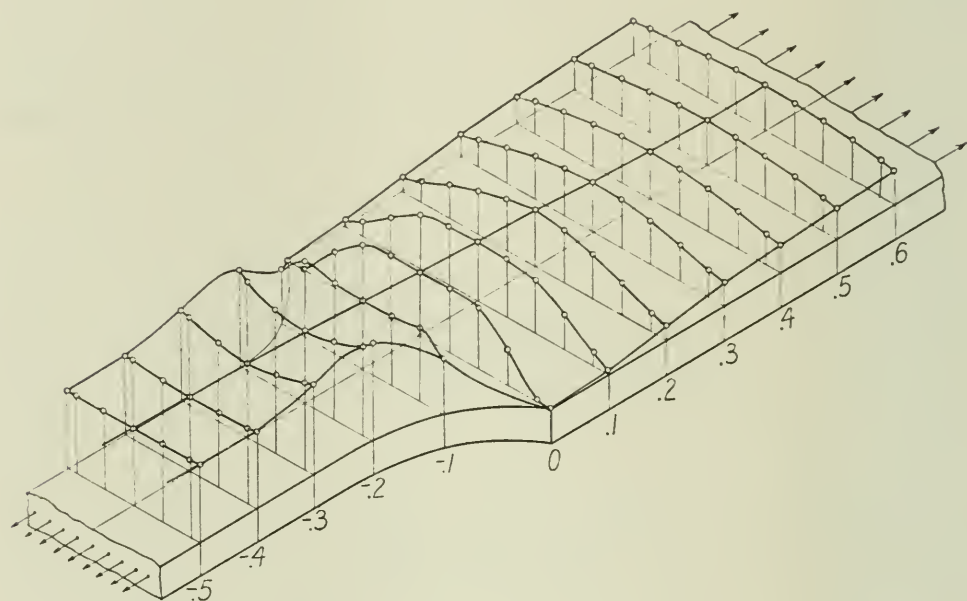


Fractional part of a test bar in simple tension for various ratios of the length D to the breadth b when the radii at the ends are varied.

than the mean tension and becomes so great with small radii that a brittle specimen tends to break at this section owing to the fact that the elastic stress distribution tends to continue right up

to the breaking point. In a ductile specimen, however, the distribution changes rapidly and tends to equalize after the yield point is passed, as you now observe in the polariscope, and in consequence ductile materials are not so prone to fracture at this section as if the elastic distribution continued. Fig. 24 shows approximately to scale the axial distribution at the ends of one form of tension test bar recommended by the British Standards Committee of The Institution of Civil Engineers,¹⁶ and you will

FIG. 24.



Drawing of the longitudinal stress distribution at the enlarged end of a tension test bar of the British Standards Committee.

notice that one of the peculiarities of the distribution is that in the narrow part the stress tends in general to become a maximum at the edges, while in the wider part the stress tends to a maximum at the centre. Unless, however, the ends are very wide compared with the central portion, it is found in this case that complex stress does not penetrate into the gauge length. The distribution of stress in any other form of tension member of plate form can be measured in a similar fashion and it may be added that in tension members of circular cross-section it has been shown experimentally¹⁷ that complex stress tends to penetrate further into the regions of the gauge length than for the corresponding case of a flat member having the same contour.

¹⁶ Appendix (24).

¹⁷ Appendix (24).

I need hardly point out that the results of these investigations emphasize the danger of relying on tests made on very short specimens, which may be of such a form that it is impossible to produce a pure tensional stress in them by a direct pull.

The Stress Distribution in Cement Briquettes.—Another form of test piece, the cement briquette, is of particular interest and importance to the civil engineer, since the manufacture and use of cement has an international character like steel, and there is no doubt that for both materials the establishment of standard tests of scientific precision, acceptable in all countries, would have a far-reaching effect on trade and commerce between them. Research on this subject has been in progress for some time at University College in order to supplement some earlier work¹⁸ on the same subject, and I take this opportunity of thanking my two research students, Messrs. Anderson and Fukuhara, for their valuable help in making measurements, which I now propose to discuss.

It is at once evident, from what has been described in the last lecture, that the stress distribution in a cement briquette must be of a very complex character. The loads are applied very obliquely to the contour at four points and the shape of the briquette is evidently one which invites complexity. This is at once evident from the lines of principal stress in the British standard form in which the contact loads applied by the grips produce a complicated stress system which would be practically impossible to unravel except by experiment.

At the time of the early experiments in 1913 it was not possible to measure the stress distribution completely, but an attempt was made to find the stress difference ($p - q$) across the minimum and principal section, and thereby to fix the relation between the maximum stress there and the mean applied load, since at the contour q must be zero at every place untouched by the grips. Some earlier measurements on a British standard briquette indicate that this maximum stress is about 1.75 times the value of the mean average stress across the section, and in the standard American form of that date the corresponding value was found to be 1.70 while in the Continental form it appeared to rise to about 1.95 times the mean stress.

These measurements have been repeated and amplified

¹⁸ Appendix (13).

recently, so that it is now possible to give a better idea of the actual stress systems at the central sections of each form, and Fig. 25 shows the distribution obtained at the minimum sections of each briquette. As will readily be observed the distinctive feature of the distribution in each case is an extremely variable tension p across the minimum cross-section accompanied by a variable cross-stress q at right angles of considerable magnitude. In the British form, for example, with a load giving a mean average stress of 500 pounds per square inch, the highest value of p at the outer contour is 870 pounds per square inch, or 1.74 times the value of the mean stress, which sinks to 405 pounds per square inch at the centre or slightly more than 80 per cent. of the mean average value. In addition to this stress there is a cross stress which rises rapidly from a zero value at the contour to a value of about 235 pounds per square inch for the central six-tenths of the cross-section, so that the manner of loading and the form of the section calls into play a cross stress of 47 per cent. of the mean average stress due to the pull.

We see, therefore, that a member of this form is certainly not in pure tension, and the color bands which are observed on the model indicate this quite clearly.

The standard French briquette shows a much more complicated distribution owing to its different shape and especially to the circular indentations at the waist.

In an actual test of this later form, shown in the figure, a mean average stress of 470 pounds per square inch develops a maximum tensional stress p of approximately 1000 pounds per square inch or 2.13 times the average stress, sinking to a minimum value at the centre of 300 pounds per square inch, that is 64 per cent. of the average value. In other experiments the ratio of the maximum stress p to the average value was found to be 2.05, 2.06 and 2.14, so that it appears very likely that this ratio is in the neighborhood of 2.10 and therefore higher than the earlier value already quoted. The stress system described above is also accompanied by a cross stress, which rises to its highest value near the end of the cross-section and has a slightly less minimum value at the centre of about 260 pounds per square inch or 55 per cent. of the average pull applied and not a great deal less than the tensional pull across the section. We have therefore, as before, a highly complex system of stress at the

cross-section for which the specimen is designed to fracture, as you now see on the screen, and if anything like the same stress system prevails in the actual briquette, we cannot hope to learn anything very definite of the tensile properties of cement under such a complicated system of stresses in it.

It is of interest here to note that French engineers have long been alive to the fact that the distribution across the central section is far from uniform and Durand Claye¹⁹ has proposed an ingenious approximate solution based on some elementary principles, in which he obtains a curve of distribution with pronounced maximum values at the ends of the section.

Having now described the main features of the stress distributions in British, American and French standard briquettes, it is evident that there is a great deal of work still to be done before any practical proposals can be adopted to obtain international uniformity in testing cement.

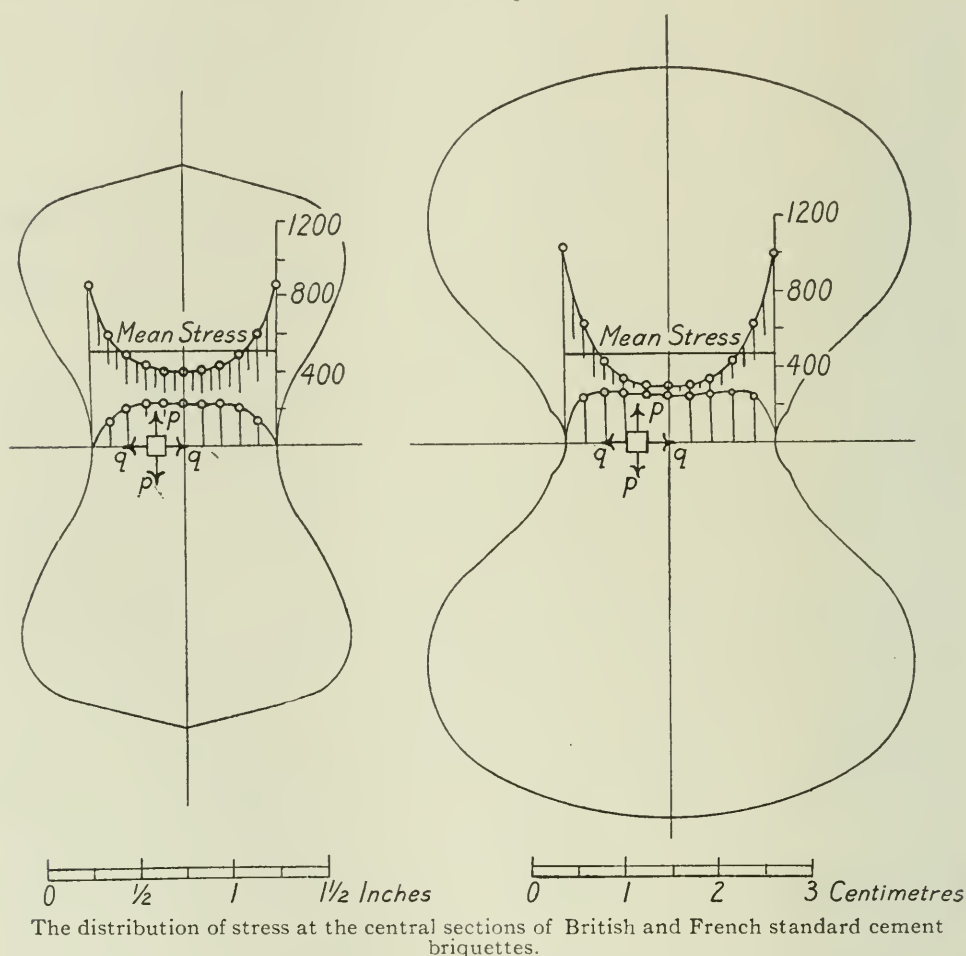
It is important to show that the stress distribution in a cement briquette is similar to that in a transparent model and recent experiments show that the sum of the principal stresses ($p + q$) at the waist are almost exactly the same as those found in a transparent model when the briquette has been made for some time. This is what may be expected, for it is very probable that the stress in a cement briquette of considerable age is of exactly the same kind as experiments on transparent models show, since old cement has very perfect elastic properties. The fact that sound vibrations are transmitted very readily through cement partition walls and floors show this, and in another direction it has been proved²⁰ that such cement possesses very perfect thermo-elastic properties. This latter property is not, however, possessed, or only imperfectly so, by cement which has been recently molded, so that so far as this evidence can be taken into account it points to the conclusion that briquettes tested at the end of a week and a month, as is sometimes provided for in standard specifications, will not be under exactly the same type of stress as transparent models show. They are in fact most probably in a semi-elastic condition in which, as all the evidence we possess shows, the stress distribution is less variable than in the purely elastic state,

¹⁹ *Annales des Ponts et Chaussées*, Tome 9, serie 7, June, 1895.

²⁰ "The Relation of Thermal Change to Tension and Compression Stress," E. G. Coker and C. M. McKergow, *Trans. Royal Soc. of Canada*, 1904.

so that any provisions found necessary from experiments on elastic bodies will more than cover the requirements we seek. The older the briquette the more nearly the stress distribution approximates to that of the elastic condition of the transparent model. The chief bar, however, to uniformity appears to be in the varying shapes of the briquettes themselves, but it does not appear to be

FIG. 25.

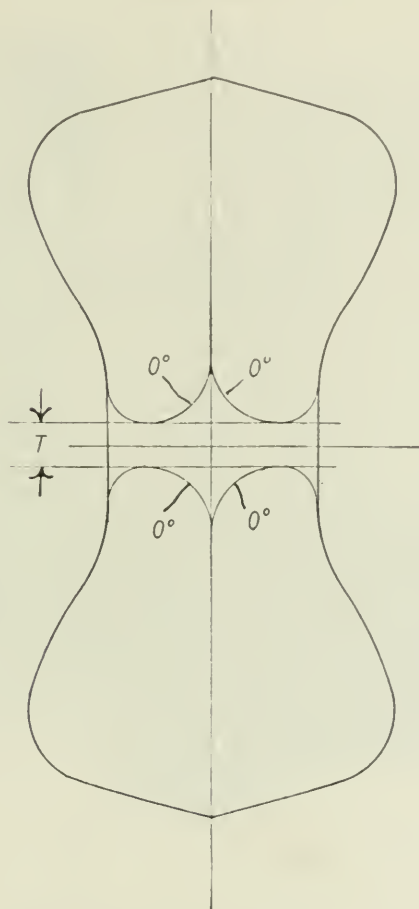


impossible to devise a simple means whereby this difficulty can be overcome without the necessity of a wholesale scrapping of existing testing machinery. Briefly, my proposal is to examine how far uniformity of testing can be obtained by maintaining in every case the existing forms of the ends and lengthening the central part by the addition of a parallel part of the least possible length which will satisfy the condition that the stress in that part is a uniform tension. Thus if we take the British standard briquette (Fig. 25) and introduce into it a definite parallel

length, the part in pure tension is at once defined by the zero isoclinics as shown in Fig. 26.

Having established this length T by experiment, and this has already been done, it is a simple matter to make the length in pure tension any quantity considered desirable, and this need only be a small fraction of an inch. Further experiment will be

FIG. 26.



Proposed modified form of the British standard cement briquette to give uniform tensional stress at the central cross-section.

necessary to find in the cement briquette the stress distribution at the waist at various ages. It has been established by recent measurements that there is uniformity of lateral contraction under load in each type of briquette lengthened in this way, thereby indicating the probability that uniform tension exists at these central cross-sections.

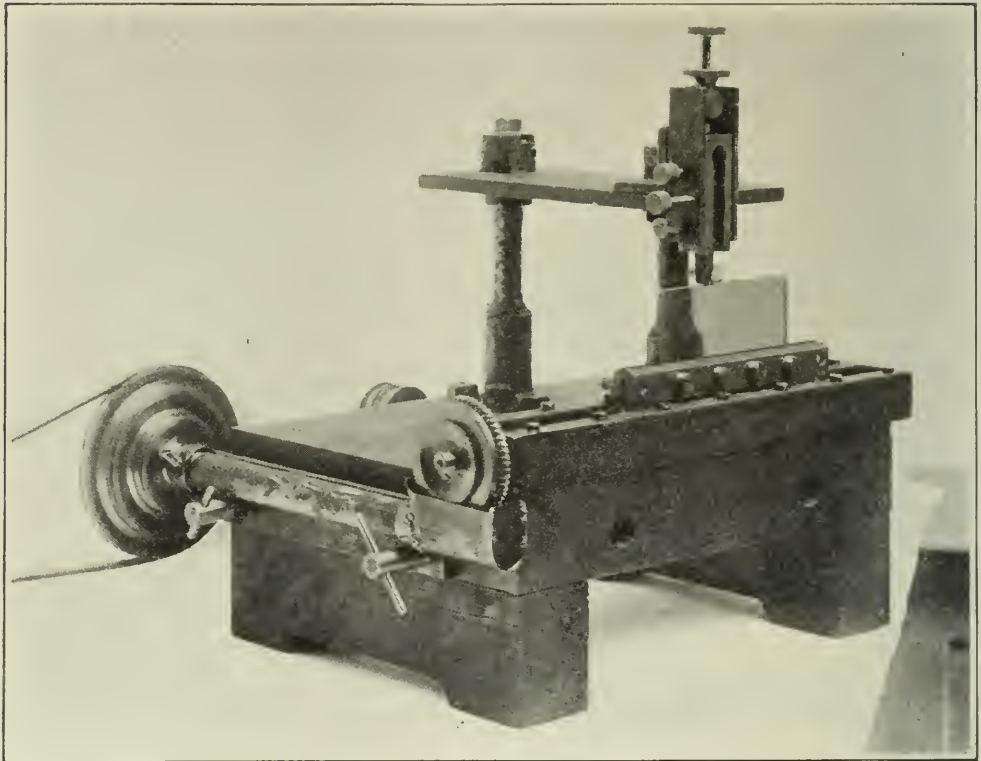
Should there be no further difficulties it would only be necessary to alter the molds now in use to obtain not only uniformity in the comparison of results, but also a real tension test of cement,

which there is some reason to believe has never yet been attained under existing conditions, owing to the variable tension at the waist, and the want of correspondence of this variability in briquettes of different patterns.

THE ACTION OF CUTTING TOOLS.

The problems of contact stress described in the former lecture lead on naturally to the vastly important subject of the action

FIG. 27.



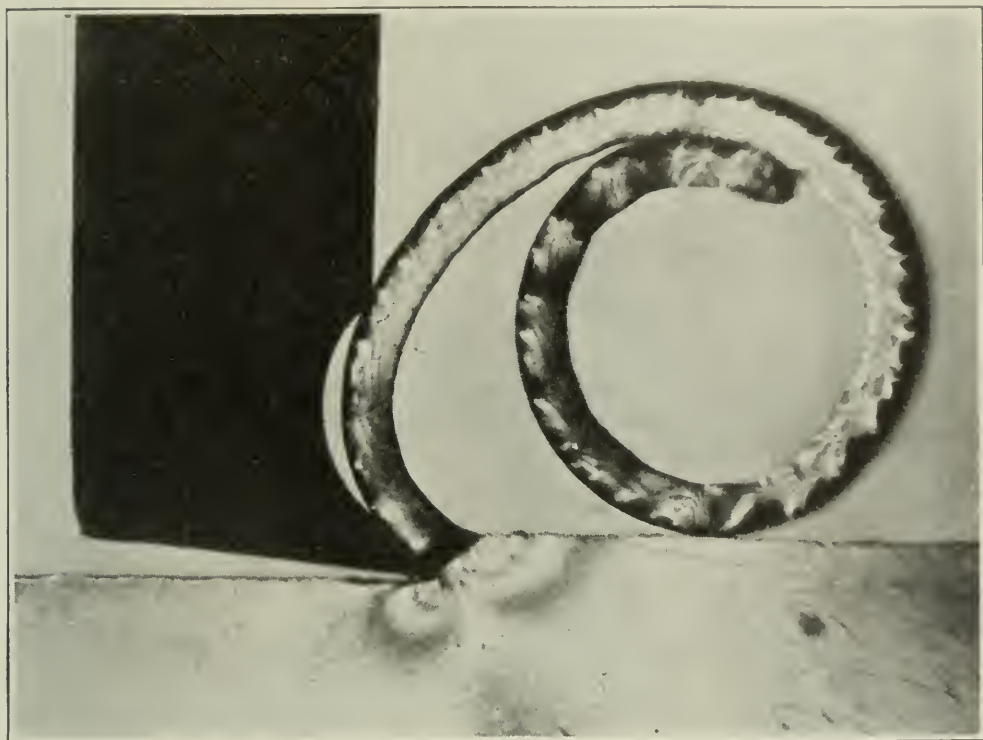
Machine for photo-elastic experiments on planing tools.

of cutting tools, and it is proposed in the remaining time to describe some recent work which was undertaken at the suggestion of Sir John Dewrance, the Chairman of the Cutting Tools Research Committee of The Institution of Mechanical Engineers, in which the action of glass and steel tools when cutting transparent materials has been examined by photo-elastic experiments.

For this purpose it has been necessary to construct special machines which will allow of this form of experiment, and a very simple one is shown in Fig. 27 for studying the action of a planing tool. For this purpose a strip of transparent material

is mounted on a slide rest, the leading screw of which is rotated by gearing operated from a small motor. For convenience the tool is secured in a suitable head having a micrometer feed to give any desired depth of cut, and also arranged to allow the tool to be reversed for cutting on the return stroke. The dispositions of the various parts of the machine are such that all the necessary

FIG. 28.

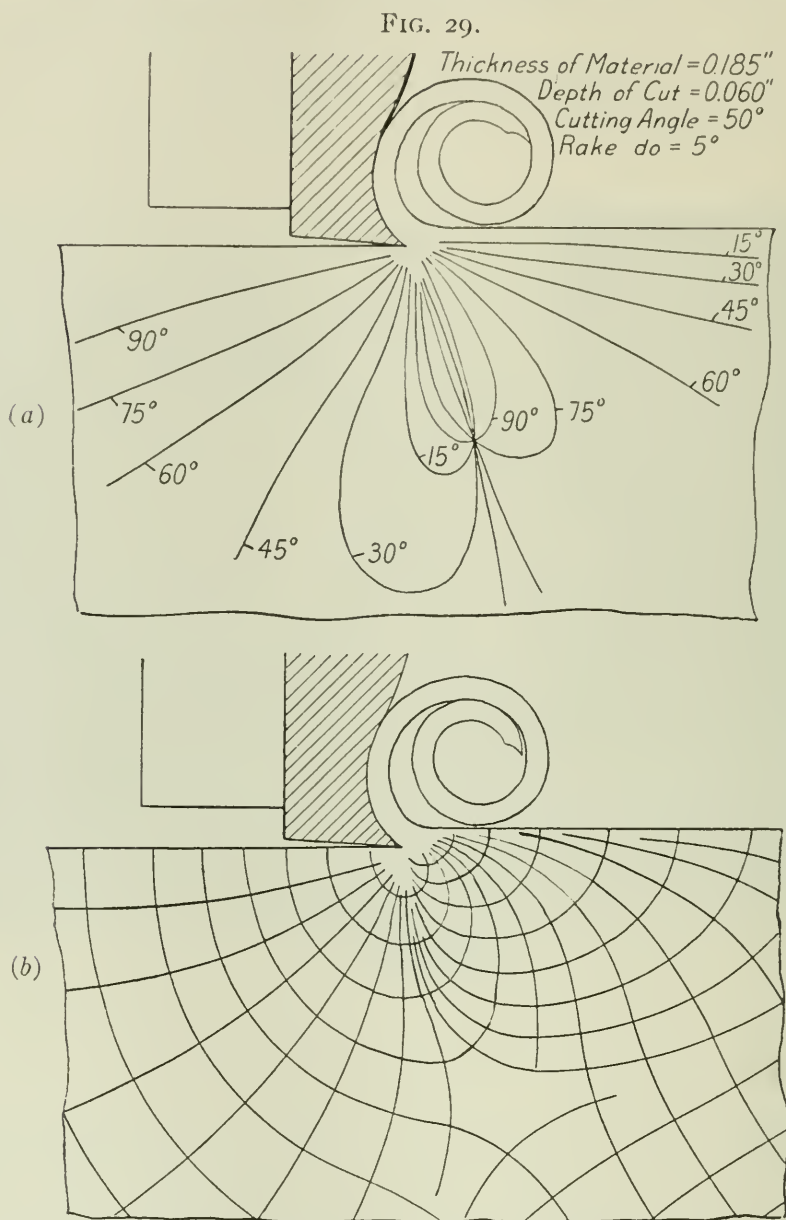


A steel planing tool operating on transparent nitro-cellulose.

measurements for ascertaining stress distribution can be made up to nearly the yield point of the material.

The general appearance of a plate under the action of a fairly well-ground cutting tool is shown in Fig. 28, in which it will be observed that the shaving removed exhibits the most intense permanent stresses which, however, are less than those experienced at or near the cutting edge of the tool, since there the colors disappear entirely and a black patch is visible which remains stationary in time during the whole of the cut. It will also be noticed that the further curling up of the shaving intensifies the stress effects at its tail. The main points of interest are, however, the stresses produced in the work and the tool.

As regards the former it will be noticed that color bands spring from near the point of the tool and in this instance form two distinct lobed systems approximately circular in form and sepa-

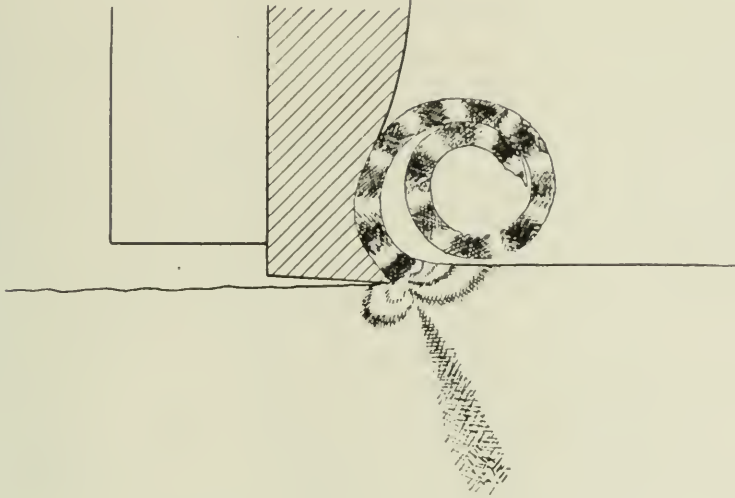


rated by a black band or brush. The optical effects in fact correspond somewhat to those shown in Fig. 17, if a diagonal plan of division *AB* is drawn through the centre of the latter and the upper part removed.

All these color phenomena appear stationary in time provided

the tool remains very sharp, but if the edge becomes at all blunt the color bands have an oscillatory motion and wax and wane in a very marked way. In order to find out what distribution of stress these color bands correspond to, a number of measurements have been made along radial lines from the point of the tool, and these show that the stress system in the area of the plant in front of the tool and black brush is roughly that of radial compression varying inversely as the distance from the point of the tool and directly as the cosine of the angular displacement from the centre line of the black brush referred to above. In the

FIG. 30.

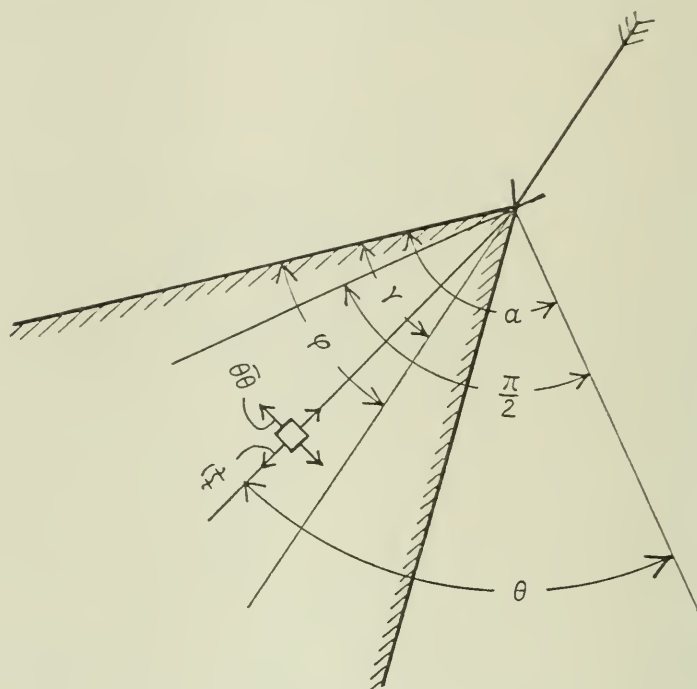


The effect of a badly ground planing tool.

corresponding area to the left of this the measurements indicate a radial tensional distribution of the same nature. It is, however, apparent that this description is only a first approximation to the actual conditions, since, if it were exactly correct, the isoclinic curves would be radial lines and coincide with one system of principal stress lines, the other set being circles with the point of the tool as centre. Actually, however, the isoclinics are curves, which bend round and intersect on the dark brush in a rather complicated fashion, as Fig. 29 shows, and the lines of principal stress are correspondingly complicated in the same area. There are in fact minor principal stresses distributed over the plate area in the neighborhood of the tool point, which must be regarded as additions to an approximately radial system of stresses such as would be caused by the tool exerting a concentrated pressure on the plate at an angle to the radius.

The behavior of a badly ground tool is still more complicated, as it appears to act like a wedge driven into the material so as to break off the shaving by a series of intermittent actions of a cyclical nature. This type of cutting, if it may be dignified by such a name, is shown in Fig. 30, in which it will be seen that the shaving has black patches separated by light colored areas. Observations show that these black patches are due to the upper

FIG. 31.



Theory of stress distribution in a tool making light cuts.

face of the tool bending back the shaving until it is broken away at these places, accompanied by a notable augmentation of the color bands until the shaving is separated from the plate, when the color bands contract and the work advances for a brief interval until it is again arrested by a further resistance due to the necessity of a further separation. The tearing away of the shaving leaves the edge of the plate with an irregular, wavy outline, which only roughly approximates to a truly flat surface.

The Stress Distribution in a Cutting Tool.—Experiments on glass tools appear to show that the stress system in the tool is possibly of a simple type, since, as can be observed, there are

bands of color springing from the point of the tool, which appear to indicate that there is only radial stress in it of the type

$$\widehat{rr} = \frac{2 C \cdot \cos (\alpha - \varphi)}{r} \quad (12)$$

where α is the angle which the cutting edge makes with the direction of maximum stress, and φ is the angle which this latter edge makes with the direction of the load concentrated at the point of the tool (Fig. 31).

If this be the case, the total component of stress measured in the direction of the zero radius is

$$\int_{\alpha-\gamma}^{\alpha} \widehat{rr} \cdot \cos \theta \cdot r \cdot d\theta = C \{ \gamma + \cos (2\alpha - \gamma) \cdot \sin \gamma \} \quad (13)$$

and in the direction at right angles

$$\int_{\alpha-\gamma}^{\alpha} \widehat{rr} \cdot \sin \theta \cdot r \cdot d\theta = C \{ \sin (2\alpha - \gamma) \cdot \sin \gamma \} \quad (14)$$

and the force P at the apex is therefore

$$P = C \sqrt{\{ \gamma + \cos (2\alpha - \gamma) \cdot \sin \gamma \}^2 + \{ \sin (2\alpha - \gamma) \cdot \sin \gamma \}^2} \quad (15)$$

while its direction is given by

$$\tan (\alpha - \varphi) = \{ \sin (2\alpha - \gamma) \cdot \sin \gamma \} / \{ \gamma + \cos (2\alpha - \gamma) \cdot \sin \gamma \} \quad (16)$$

These results, due to Michell,²¹ have been shown to apply very closely to the case of a tool when the action is at or near the cutting edge and it seems probable, except for heavy cuts, that this is the ruling type of stress distribution at and near the cutting edges when well supported from the rear face of the tool.

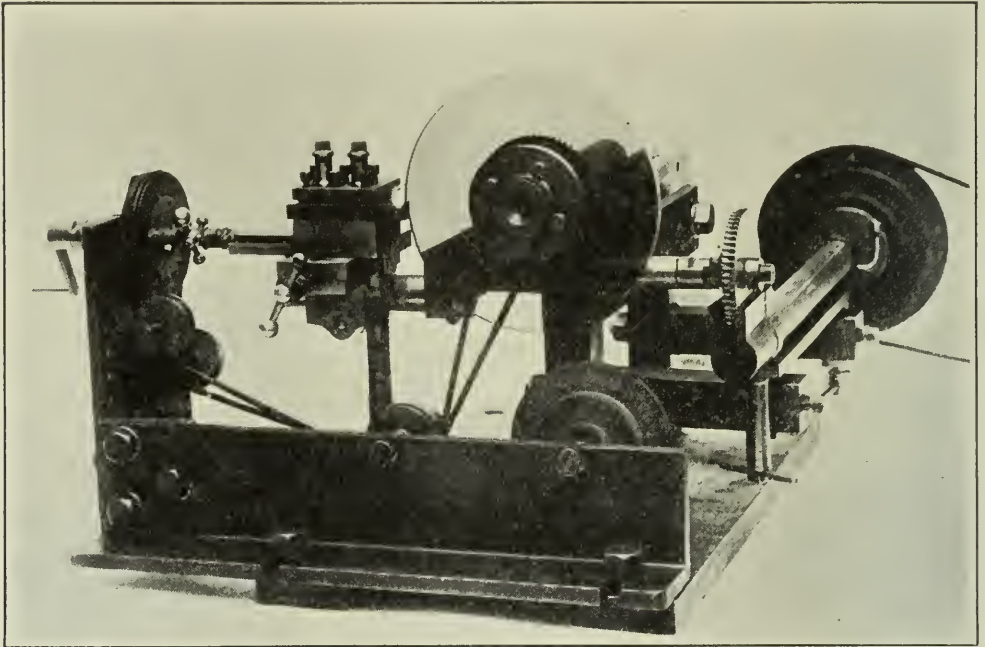
Similar experiments on turning tools have also been carried out in a small lathe specially built to allow a beam of light to be transmitted through the work and the tool, and the general construction of this piece of experimental apparatus is shown in Fig. 32, in which the main spindle of the lathe carrying a transparent disc is revolved by a motor, which latter is belted up to a first motion shaft, driving a second motion shaft by a worm gear. This second shaft is geared to the lathe spindle by a second worm-gear drive as indicated, and the disc turns at a sufficiently low speed to allow all the optical and lateral measurements to be made by modifications of the apparatus already described.

²¹ *Proc. London Math. Soc.*, 34 (1902). Appendix (34).

An ordinary form of compound slide rest is used to carry the tool, with the addition of a backstop to prevent radial slip, and there is also an automatic feed for the lower slide. This feed is accomplished by a belt connecting a three-sheaved pulley on the second motion shaft, with a pulley on the screw shaft of the slide rest.

This latter arrangement is found to give a very uniform radial feed when adjustable pulleys are provided for regulating

FIG. 32.



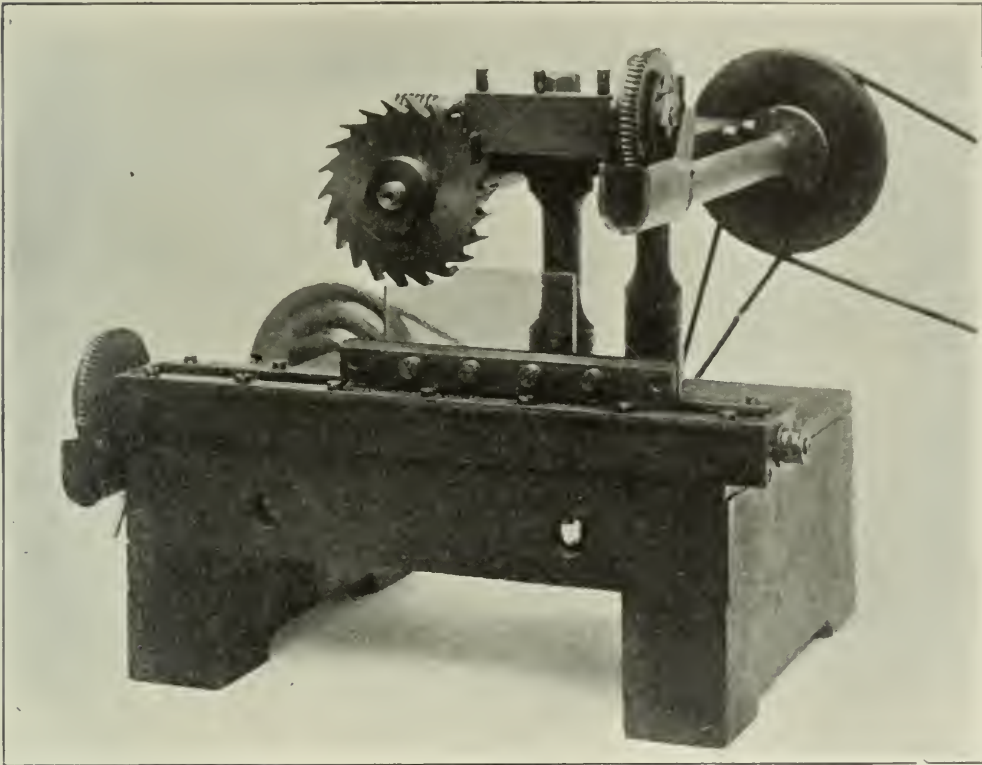
Experimental lathe for photo-elastic experiments with turning tools.

the belt tension, and the general phenomena observed are very similar to those described here in relation to planing tools and have already been very fully described.²² A more complicated case has been examined recently in which several cutting edges are acting simultaneously as in milling operations. For this purpose another machine was constructed, as shown in Fig. 33, in which, with the exception of the tool-holder, the principal elements of the two former machines are combined to allow the rotary cutter to operate upon a transparent plate secured to a small table which is advanced uniformly by a worm-gear system operated from the main shaft and actuating the screw feed of the slide rest in the foreground. It is of interest to note that in this form of

²² Appendix (34).

cutting action the shaving grows in thickness as the cut proceeds owing to the fact that the path of the point of the tool is a trochoidal curve, and while the horizontal intercepts between adjacent curves are constant, the radial intercepts increase with the angular motion of the cutter. It is also of interest to note that the final surface produced by a milling cutter operating in a straight line is essentially of a wave form, approximating, it is

FIG. 33.



Milling machine for photo-elastic experiments.

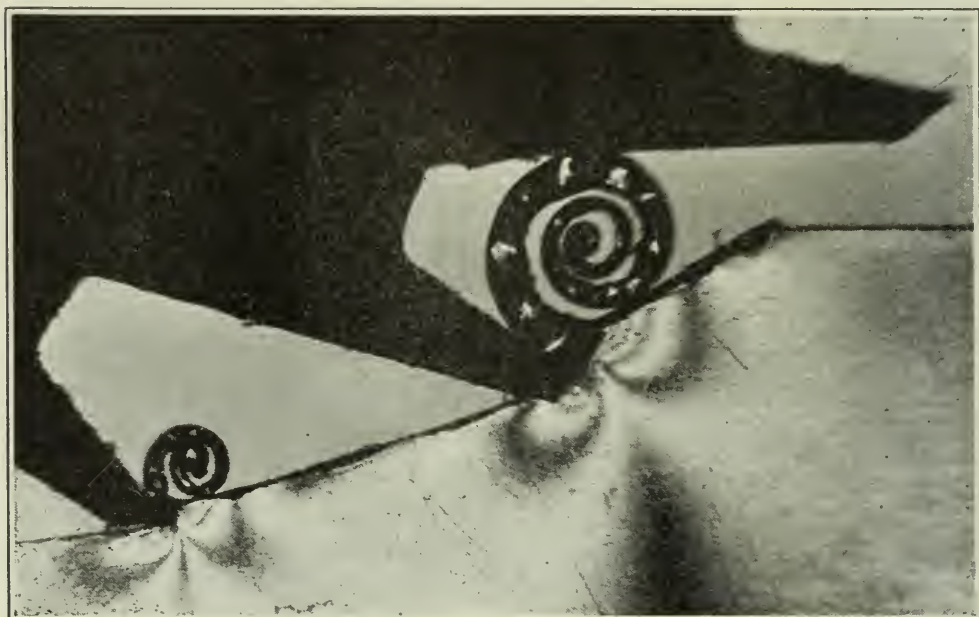
true, to a plane when the rotation of the cutter and the feed are suitably arranged, but never quite reaching the ideal flat surface.

As may be expected, the presence of two or more cutting edges operating at one time to remove shavings of gradually increasing thickness is somewhat complicated, as will be seen in Fig. 34, in which it will be observed that the stress color bands observed previously again reappear, but the stress intensity varies somewhat with the depth of cut. Thus in the foremost operating cutter intensity is very marked as compared with the cutting edge on the extreme left, although the stress systems round each point are similar. At the contour between them a point must be reached

at which the compression stress caused by an advancing tooth is reduced to zero by the tensional stress caused by the drag of the tooth in advance, and the small black patch on the contour and somewhat to the left of the centre indicates the position of this zero stress. Measurements of the stress distribution in the plate confirm this.

The appearance of the shavings removed are also of interest, since the alternations of light and dark patches show that the

FIG. 34.



A milling cutter in action.

material is being wedged off with little or no true cutting action. The cut surface obtained is not, however, found to be so rough as in surfaces operated upon by one cutter and giving a similar action, since the final surface produced is an aggregation of small faces produced at the commencement of the cut when the shaving is thin and the wedging-off action is not so pronounced.

Although much other work has been carried out on these lines in an attempt to understand the action of cutting tools, this brief description is probably sufficient to show that photo-elastic research is a means which is fruitful of results, even in so old and well-cultivated a field of experimental investigation as that of the action of cutting tools.

APPENDIX.

PAPERS ON PHOTO-ELASTICITY.

BY PROF. E. G. COKER AND COLLABORATORS.

- (1) "Note on the Application of Polarized Light to Determine the Condition of a Body under Stress," Profs. S. P. Thompson and E. G. Coker, *B. A. Report*, 1909.
- (2) "The Optical Determination of Stress," *Phil. Mag.*, Oct., 1910.
- (3) "Photo-elasticity," *Engineering*, Jan. 6, 1911.
- (4) "The Determination, by Photo-elastic Methods, of the Distribution of Stress in Plates of Variable Section, with Some Applications to Ships' Plating," *Trans. Inst. Naval Architects*, 1911.
- (5) "The Use of Polarized Light as an Aid to Determining the Effect of Stress in Engineering Materials," *Proc. Sheffield Soc. Eng. and Metal.*, 1911.
- (6) "An Optical Determination of the Variation of Shear Stress in a Thin Rectangular Plate Subjected to Shear," *Proc. R. S.*, 1912.
- (7) "Color Photography of Internal Stress in Bodies of Engineering Forms," West of Scotland Iron and Steel Institute, 1912.
- (8) "The Determination of the Stresses in Springs and other Bodies by Optical and Electrical Methods," *B. A. Report*, Section G, 1912, and *Engineering*, Sept., 1912.
- (9) "The Design and Construction of Large Polariscopes," Profs. E. G. Coker and S. P. Thompson, *Proc. Optical Convention*, 2, 1912.
- (10) "The Applications of Polarized Light to Mechanical Engineering Problems of Stress Distribution," *Proc. Inst. Mech. Engineers*, 1913.
- (11) "Column Testing Machine," *Proc. Phys. Soc., Lond.*, 1913.
- (12) "The Effects of Holes and Semi-circular Notches on the Distribution of Stress in Tension Members," *Proc. Phys. Soc., Lond.*, 25, Part II, 1913.
- (13) "The Distribution of Stress at the Minimum Section of a Cement Briquette," International Association for Testing Materials, New York Congress, 1913.
- (14) "The Measurement of Stresses in Materials and Structures," Cantor Lectures, Royal Society of Arts, 1913.
- (15) "The Distribution of Stress Due to a Rivet in a Plate," Prof. E. G. Coker and Mr. W. A. Scoble, *Trans. Inst. Naval Architects*, 1913.
- (16) "The Stress Distribution in Short Compression Members," Profs. E. G. Coker and Filon, *B. A. Report*, 1914.
- (17) Presidential Address to Section G (Engineering) of the British Association at Sydney, *B. A. Report*, 1914.
- (18) "Experimental Determination of the Distribution of Stress and Strain in Solids," Profs. Filon and E. G. Coker. Report of the Committee on Stress Distributions in Engineering Materials, *B. A. Report*, 1914.

- (19) "Gli sforzi interni nei materiali da costruzione determinati mediante la luce polarizzata," Prof. E. G. Coker, *Annali Societa d'Ingegneria e Architetti*, 1916.
- (20) "Il metodo sperimentale del Prof. E. G. Coker per determiniane gli sforzi interni nei materiali da costruzione mediante la luce polarizzata, Prof. L. Luiggi, *Annali Societa d'Ingegneria e Architetti*, 1916.
- (21) "Polarized Light and its Applications to Engineering," Friday Evening Discourse Royal Institution, 1916.
- (22) "The Stress in the Fillets of a Crank Shaft," Report on the Materials of Construction Used in Aircraft, Aeronautical Research Committee, 1920. Edited by Prof. C. F. Jenkin.
- (23) "Photo-elasticity for Engineers," *Proc. Inst. Autom. Engs.*, 1917.
- (24) "Photo-elastic Measurements of the Stress Distribution in Tension Members Used in the Testing of Materials," *Min. Proc. Inst. Civil Eng.*, 208, 1918-19.
- (25) "Photo-elastic and Strain Measurements of the Effects of Circular Holes on the Distribution of Stress in Tension Members," Prof. E. G. Coker, Messrs. K. C. Chakko and Y. Satake, *Proc. Inst. Engineers and Shipbuilders in Scotland*, 1919.
- (26) "The Stress-strain Properties of Nitro-cellulose and the Law of its Optical Behavior," Prof. E. G. Coker and Mr. K. C. Chakko, *Phil. Trans. R. S.*, 1920.
- (27) "The Effects of Holes, Cracks and Other Discontinuities in Ships' Plating," Prof. E. G. Coker and A. L. Kimball, *Trans. Inst. Naval Architects*, 1920.
- (28) "Tension Tests of Materials," *Engineering*, Jan., 1921.
- (29) "Stress Concentration Due to Notches and Like Discontinuities," Prof. E. G. Coker and Dr. Paul Heymans, *B. A. Report*, 1921, also reprinted in *Engineering*.
- (30) "Contact Pressures and Stresses," Prof. E. G. Coker, K. C. Chakko and M. S. Ahmed, *Proc. Inst. Mech. Engineers*, 1921.
- (31) "The Effects of Scratches in Materials," Engineering Conference, The Inst. Civil Engineers, 1921.
- (32) "Recent Researches in Photo-elasticity," *Proc. Sheffield Soc. Eng. and Metal.*, 1921.
- (33) "Photo-elasticity for Engineers," six lectures delivered at the Research Laboratory of the General Electric Company, Schenectady, New York, and afterwards published in General Electric Company's Magazine, 1920-21.
- (34) "An Account of Some Experiments on the Action of Cutting Tools," Prof. E. G. Coker and K. C. Chakko, *Proc. Inst. Mech. Eng.*, 1922.
- (35) "Curved Beams, Rings and Chain Links" (Honorary Members' Lecture), *Jour. Jr. Inst. Eng.*, 1922.
- (36) "Des Recherches Récentes sur la Photo-Elasticimétrie ayant rapport à son application dans les Problèmes Posées en Construction," La Société des Ingénieurs Civils de France, 1922; see also *Engineering*, June 16, 1922.

THE VALUES OF THE ELECTRICAL MOMENTS OF THE ATOMS AND THEIR CONNECTION WITH OTHER QUANTITIES.*

BY

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SINCE an atom consists of a number of electrons distributed around a positive nucleus, its electrical effect at a distant point would be equivalent to an electrical doublet. The force between two atoms, which may be either an attraction or a repulsion, depending on the way the representative doublets face each other, would, accordingly, be proportionate to the product of the electrical moments of the atoms, and inversely proportional to the fourth power of their distance of separation. When the atoms or molecules are free to move about as in a gas or liquid their electrical doublets would tend to arrange themselves with respect to each other, as the writer has pointed out,¹ so that the potential energy would be a minimum. The outstanding force would therefore be attraction, and if repulsion occurs, it would be as small as possible. Thus there would be an association between the directions of the axes of the atomic doublets at every instant, though all directions of the axis of each doublet are equally probable, since the substance as a whole does not possess any polarity. But the attraction between two atoms or molecules in a substance at constant temperature would not follow the inverse fourth power law, since the orientation of the molecules with respect to each other at any instant would depend on the nature and number of collisions they undergo per second, which would depend on the density and temperature of the substance. The attraction between two atoms or molecules of electrical moment M corresponding to the average distance of separation z of the molecules of the substance would accordingly be given by

$$\psi(z, T) \cdot \frac{M^2}{z^4},$$

* Communicated by the Author.

¹ *Phys. Rev.*, **18**, 4. p. 303.

where the function $\psi(z, T)$ expresses the effect of molecular collision on the law of molecular attraction. The effect of molecular collision in interfering with the tendency of the molecules to set themselves so that attraction is the outstanding force, and that it be as great as possible, will evidently increase with increase in temperature. We would therefore expect that the function $\psi(z, T)$ should decrease in value with increase in temperature for a constant value of z .

The writer has deduced² from various experimental data that the attraction between two molecules is given by

$$\phi\left(\frac{z}{z_c}, \frac{T}{T_c}\right) \frac{(\sum c_a)^2}{z^5},$$

where $\sum c_a$ denotes the sum of a number of atomic constants each of which is very approximately proportional to the square root of the atomic weight of the atom to which it refers, z_c is the distance of separation of the molecules at the critical point, and T_c the critical temperature. The function ϕ does not appear to vary much with either z or T . It follows from this result that the electrical moment of an atom is proportional to the square root of its atomic weight, and that the moment of a molecule is equal to the sum of the moments of its atoms. This would explain, as the writer has shown,³ the stopping power law of the α particle. It also follows from the above law that the effect of molecular collision in modifying the inverse fourth power law is represented by the factor $\phi\left(\frac{z}{z_c}, \frac{T}{T_c}\right) \frac{1}{z}$ in the law of molecular attraction.

The square root of the atomic weight of an atom is very approximately proportional to the two-thirds power of its atomic number, according to Glasston.⁴ And since the atomic number N is equal to the number of elementary electrical charges associated with the atom, the distance of separation x of the two charges in the representative electrical doublet of the atom, is given by

$$\begin{aligned} xNe &= k_1 N^{2/3} \\ \text{or} \quad x &= k_2 N^{-1/3} \end{aligned} \tag{1}$$

where k_2 is a constant. Thus x decreases with increase of the atomic weight of an atom. This is probably due to the fact that

² *Phil. Mag.*, May, 1910, p. 783; Jan., 1911, p. 83. *Proc. Camb. Phil. Soc.*, 16, pt. 7, p. 583.

³ *Loc. cit.*

⁴ *Phil. Mag.*, 43, p. 477.

the larger the atom the more symmetrical its electrons are likely to be distributed around the positive nucleus.

The forces between atoms and molecules have been explained by Debye ⁵ along electrical lines by assuming that during their motion of translation and collision with each other they undergo contractions and expansions successively in such a manner that attraction would be the outstanding force. But it is evident from the theory proposed by the writer that such an assumption need not be introduced, is, in fact, quite unnecessary. Nevertheless, such expansions and contractions may, and probably do, take place, but they would not form the dominating factor in determining the nature of the forces the molecules exert upon each other.

It can easily be shown from the facts that the factor $\psi(z, T)$ in the law of attraction is not a constant but a function of z and T . Thus if we assume that it is a constant, it can easily be shown ⁶ that the internal heat of evaporation L of a liquid is given by

$$L = a (\rho_1 - \rho_2) \quad (2)$$

where ρ_1 denotes the density of the liquid and ρ_2 that of the vapor, and a a constant which depends on the nature of the liquid. Table I, taken from the paper quoted, gives the values of $L/\rho_1 - \rho_2$

TABLE I.

Ethyl Oxide.				Carbon Tetrachloride.				Methyl Formate.			
T	$\frac{L}{\rho_1 - \rho_2}$	T	$\frac{L}{\rho_1 - \rho_2}$	T	$\frac{L}{\rho_1 - \rho_2}$	T	$\frac{L}{\rho_1 - \rho_2}$	T	$\frac{L}{\rho_1 - \rho_2}$	T	$\frac{L}{\rho_1 - \rho_2}$
273	117.1	393	100.2	273	29.6	473	25.3	273	112.9	443	89.5
313	109.9	433	93.4	393	27.4	513	24.4	323	107.6	483	73.4
353	104.7	460	88.7	433	26.4	553	22.1	403	95.6	496	68.1

at different temperatures for a number of substances. It will be seen that they decrease with increase of temperature.

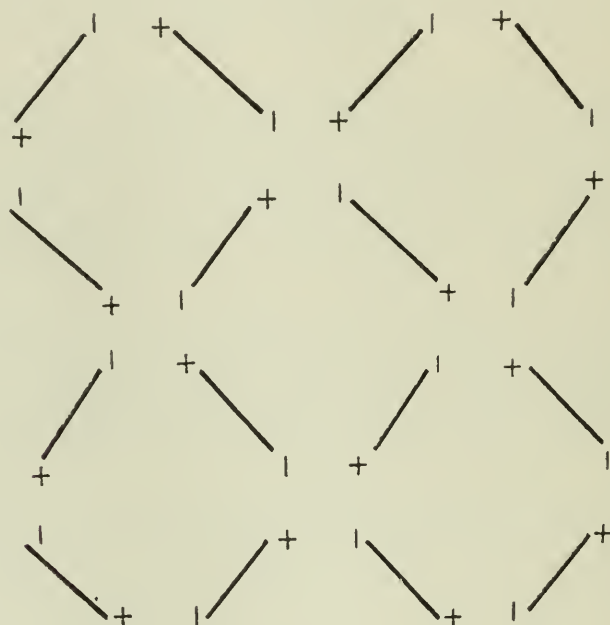
The nature of the function $\psi(z, T)$ cannot be determined from the variations of a since they are due to *simultaneous* variations of z and T . The moment of an atom or molecule cannot, therefore, be determined from data on the internal heat of evaporation for temperatures above the absolute zero. But it is possible to

⁵ *Phys. Zeit.*, 21, p. 178 (1920).

⁶ *Phil. Mag.*, Oct., 1910, p. 677.

carry this out at a temperature at, or near, the absolute zero, as will now be shown. At such a temperature the number of collisions a molecule undergoes per second with other molecules is very small, and the tendency of the molecules to set themselves so that the attraction between them is as large as possible will, therefore, be little affected. The resultant distribution of the axes of the molecular electrical doublets in space would obviously be such that the force acting on a molecule is on the average the same in any two opposite directions. It will also not be difficult to see

FIG. 1.



that the nature of the distribution would depend somewhat on the density of the substance. The average distribution may be approximately obtained without incurring mathematical difficulties.

Before proceeding to obtain this distribution, it should be pointed out that the molecules of a substance in the condensed state at the absolute zero of temperature do not strictly behave as electrical doublets, since they are in equilibrium under the action only of their forces of attraction and repulsion, on account of the absence of motion of translation. The existence of these forces would be shown by the nature of the resistance that would be encountered on expanding or compressing the substance. Since we infer from the behavior of substances at ordinary tempera-

tures that the coefficient of compression would be extremely small at the absolute zero, which naturally holds also for the coefficient of expansion, a small expansion of the substance would cause great forces of attraction between the molecules to come into play, or the molecules would behave like electrical doublets under the new conditions. Thus only over a small range of densities the molecules are not likely to behave as electrical doublets.

The average positions of the molecules in space would correspond to the points of intersection of three sets of parallel and equidistant planes at right angles to each other, since this distribution fulfils the condition that the potential energy corresponding to a given density of the substance is a minimum. Let us suppose that the axes of the doublets lie on diagonals of the cubes formed by the foregoing planes of reference in such a way that a projection of the doublets, whose centres lie on a plane, on to this plane, gives an arrangement as shown in Fig. 1, in which the projected axes are situated at right angles with opposite charges facing each other. The force acting on a doublet, which is an attraction, will evidently be the same in three directions at right angles to each other, and is as large as is possible under these conditions.

Now the attraction between two doublets lying on a plane, and making angles θ_1 and θ_2 with the line joining their centres is

$$- 3 \frac{M^2}{r^4} (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2).$$

The attraction between two doublets whose centres are situated on a line formed by the intersection of the foregoing planes of reference is therefore given by

$$+ 5 \frac{M^2}{r^4},$$

since the doublets lie on a plane and are inclined at an angle of 45° to the line joining their centres. The attraction between two doublets not lying in the same row will evidently be less than that given by the above expression. For our purpose it is necessary to obtain the average law applying to any pair of doublets. An approximation to this law is obtained from the following considerations.

Two doublets lying on the same straight line, with opposite charges facing each other, exert upon each other the attraction

$$6 \frac{M^2}{r^4}.$$

If the axes of the doublets are parallel and opposite charges face each other, the attraction is

$$3 \frac{M^2}{r^4}.$$

Thus, if a doublet is placed at the origin of a system of rectangular axes, and a doublet on each axis some distance from the origin, the attraction along one axis will be given by the first of the foregoing expressions, and that along each of the remaining two axes by the second expression, if the doublets are parallel to one of the axes and so arranged that the force is attraction. But we have seen that the average distribution of the axes of the doublets in space is such as to give the same attraction along three rectangular axes. Now we may suppose the above system of coördinates to rotate around its origin, and therefore the general representative law of attraction that may be taken to hold for any pair of doublets is *approximately* given by the mean of the foregoing expressions, which is

$$\frac{6 + 3 \times 2}{3} \frac{M^2}{r^4} = \frac{4M^2}{r^4}.$$

The attraction given by this expression is a little less than that given by the preceding investigation, as should be the case if it is to represent the average law. Since the exact determination of the average law leads to mathematical difficulties, and it is not likely to differ much from the foregoing law, this will be used in the investigations in this paper, whose main object is to determine the absolute value of the moment of an atom.

The process may be considerably shortened by using a result obtained previously by the writer. It was shown⁷ that if the attraction between two molecules or atoms is given by

$$\frac{K_1}{z^5},$$

⁷ *Proc. Camb. Phil. Soc.*, 16, pt. 7, p. 593 (1912).

where z denotes their distance of separation and K_1 a constant, the internal heat of evaporation in ergs per gram, in the particular case that the vapor obeys the gas laws, is given by

$$L = 1.58 \frac{\rho_1^{4/3}}{m_a^{1/3}} K_1,$$

where ρ_1 denotes the density of the substance and m_a the absolute mass of an atom or molecule. This expression for L involves the factor obtained by the integration of

$$\int_z^\infty \frac{1}{z^5} \cdot dz,$$

which gives

$$\frac{1}{4z^4} = \frac{1}{4} \left(\frac{\rho_1}{m_a} \right)^{4/3},$$

where

$$\left(\frac{m_a}{\rho_1} \right)^{1/3} = z$$

denotes the distance of separation of the molecules. The latent heat expression corresponding to the law of attraction

$$\frac{K_1}{z^4}$$

is therefore obtained from the foregoing expression on multiplying it by

$$\frac{1}{3} \left(\frac{\rho_1}{m_a} \right)^{1/3} \bigg/ \frac{1}{4} \left(\frac{\rho_1}{m_a} \right)^{4/3},$$

which gives

$$L = 2.106 \frac{\rho_1}{m_a^2} K_1.$$

If this equation is applied to the absolute zero of temperature we have

$$L_0 = 8.42 \frac{\rho_0}{m_a^2} M^2 \quad (3)$$

since we have just shown that

$$K_1 = 4 M^2$$

in that case, where L_0 denotes the latent heat and ρ_0 the density at the absolute zero.

TABLE II.

	v_0	T	ρ_1	L in cal.	m	I_0 in cal.	M_{1018}	$\Sigma N^{2/3}$	$\frac{M_{1020}}{\Sigma N^{2/3}}$
Iodobenzene.....	89.9	303	1.8149	53.75	203.9	83.9	3.51	38.9	9.03
Chlorobenzene.....	79.0	273	1.1278	82.90	112.5	132.2	3.08	31.4	9.77
Fluorobenzene.....	70.6	273	1.0465	81.74	96.09	138.1	2.74	29.1	9.42
Bromobenzene.....	82.2	303	1.4815	64.84	157.	107.6	3.33	35.5	9.40
Stannic chloride.....	87.	273	2.2789	33.3	260.8	57.62	3.25	40.0	8.12
Carbon tetrachloride.....	72.7	273	1.6327	48.35	153.8	81.12	2.70	29.7	9.10
Benzene.....	66.4	273	.9001	100.16	78.05	170.6	2.66	25.8	10.31
Octane.....	123.5	273	.7185	84.71	114.14	119.9	3.83	44.4	8.62
Pentane.....	80.7	273	.6454	85.85	72.10	164.4	2.77	28.5	9.71
Ethyl ether.....	72.6	273	.7362	86.16	74.	165.1	2.67	27.2	9.80
Acetone	53.2	273	.8186	131.82	58.	223.2	2.35	20.9	11.24
Carbon disulphide.....	45.	273	1.2921	82.76	76.	141.3	1.97	16.0	12.29
Sulphur dioxide.....	31.	263	1.460	86.56	64.	173.0	1.66	14.36	11.55
Carbon dioxide.....	25.5	243	1.045	65.34	44.	177.8	1.27	11.3	11.20

The value of L_0 may be obtained by extrapolation from an empirical latent heat equation. The one best suited for this purpose is

$$L = (\rho_1^2 - \rho_2^2) k_3$$

given by Batschinski⁸ and the writer,⁹ where ρ_1 denotes the density of the liquid and ρ_2 that of the vapor. At low temperatures ρ_2 may be neglected in comparison with ρ_1 . The constant k_3 may be determined by applying the equation to the substance at a temperature for which ρ_1 and L are known, and L_0 would accordingly be given by

$$L_0 = \left(\frac{\rho_0}{\rho_1} \right)^2 L \quad (4)$$

Table II contains the values of L_0 for a number of substances, and the values of L , ρ_1 corresponding to the given values of the absolute temperature T and the values of $\frac{m}{\rho_0} = v_0$, used for their calculation, where m denotes the molecular weight relative to hydrogen, and v_0 the molecular volume per gram molecule at the absolute zero of temperature. The values of L and ρ_1 were obtained from papers by Mills,¹⁰ and the extrapolated values of v_0 from a paper by Traube.¹¹ The values of L_0 thus obtained were used to calculate the values of M by means of equation (3), the results being given in the table. On examining them it will appear that the electrical moment of a molecule is equal to the sum of the electrical moments of its atoms, and that the moment of an atom is proportional to the two-thirds power of its atomic number N . Thus if the ratio $M/\Sigma N^{2/3}$ for the various molecules is obtained, it is found to be approximately a constant, as is shown by the last column of Table II. The mean value of this ratio is 10^{-19} . The electrical moment M_a of an atom is accordingly given by

$$M_a = 10^{-19} N^{2/3} \quad (5)$$

and that of a molecule by

$$M = 10^{-19} \Sigma N^{2/3} \quad (6)$$

In the foregoing investigation we have used only two assumptions which may really be classed as such, namely, that atoms and

⁸ *Ann. der Physik*, **14**, p. 305 (1904).

⁹ *Phil. Mag.*, Oct., 1910, pp. 678-682.

¹⁰ *Jour. Phys. Chem.*, **8**, p. 405 (1904), etc.

¹¹ *Phys. Zeit.*, Oct., 1909, p. 667.

molecules possess definite electrical moments in their interaction with each other, and that these moments at the absolute zero of temperature are approximately independent of the density of the substance between that corresponding to the condensed state and the vaporous state inclusive. They led to the remarkable results expressed by equations (5) and (6). These constitute, I think, strong evidence that the assumptions made are true. Every theory of the distribution of the electrons and the positive charges in an atom must therefore take into account that, at distances from the centre of the atom greater than its diameter, it behaves as if it consists of an electrical doublet.

Since the moment of an atomic doublet is $10^{-19} N^{2/3}$ according to equation (5) and it was previously expressed in this paper in the form xNe , it follows that $k_2 = \frac{10^{-19}}{e}$ in equation (1). Therefore, on taking e equal to 4.77×10^{-10} e.s.u. (Millikan's value), we obtain

$$x = 2.09 \times 10^{-10} N^{-1/3} \text{ cm.} \quad (7)$$

from this equation. The distance of separation x of the electrical charges in the representative doublet of an atom is thus much smaller than its diameter. It will be of interest to examine this result more closely. In the case of the hydrogen atom, which is supposed to consist of an electron rotating in a circle the centre of which is occupied by the positive nucleus, we have $N = 1$ and hence $x = 2.09 \times 10^{-10}$ cm. The value of x is obviously much less than the diameter of the atom, which is of the order of 10^{-8} cm. According to Bohr's investigations in connection with the origin of spectra the distance of the rotating electron from the nucleus is $.53 \times 10^{-8}$ cm. Thus, in order that the atom may behave as an electrical doublet, it is necessary that the nucleus does not occupy the centre of the circular path of the electron but a point a distance $x = 2.09 \times 10^{-10}$ cm. from the centre at right angles to the plane of motion. Strictly, the system will not be in equilibrium under these conditions according to the known laws. But this is not a very serious objection since there is a great deal of evidence along other lines that the motion of an electron in an atom does not obey the Newtonian dynamics. If the electron describes an ellipse with the nucleus at one of the foci, the atom might behave on the whole as a doublet. It is, however, more likely that the doublet effect is brought about in the way first suggested. It is also very

likely that the doublet effect of the more complicated atoms is mainly caused by the positive nuclei not occupying the foci of the paths of the moving electrons.

The inductivity of a substance, it is scarcely necessary to point out, is easily explained if its atoms and molecules behave as electrical doublets. An electric field applied to the substance would tend to set these doublets parallel to itself, while the collisions the molecules undergo would tend to interfere with this tendency, since a collision between two doublets would suddenly change the directions of their axes. The inductive effect of a substance subject to an electric field may therefore be represented by assuming that the doublets are stationary in space and set with their axes inclined at an angle to the lines of electric force depending on the intensity of the field. This angle can be calculated, knowing the magnitude of the moments of the atoms.

If it is assumed that the inductivity is caused by the atoms behaving as perfect conductors of electricity of spherical form, and v denotes their total volume per c.c., the dielectric constant K , according to the well-known Mossotti Clausius equation, is given by

$$K = \frac{1 + 2v}{1 - v}$$

or

$$v = \frac{K - 1}{2 + K} \quad (8)$$

Now when an atom of radius r is placed in an electric field of intensity H in e.s.u., a doublet of moment Hr^3 is induced whose axis is parallel to the electric lines of force. This doublet may be taken to arise from the projection of the molecular doublet on to the direction of the lines of force, and hence we may write

$$Hr^3 = M \cos \theta$$

We also have

$$= n \pi r^3 \frac{4}{3},$$

where n denotes the number of molecules per c.c., and therefore

$$v = \frac{4}{3} n \pi \frac{M \cos \theta}{H}.$$

Since all the quantities this equation contains are constants except $\cos \theta$ and H , it follows that these two quantities are proportional to each other, and we may therefore write

$$v = \frac{4}{3} n \pi M \cos \theta' \quad (9)$$

where the angle θ' corresponds to an electric field of unit intensity. From this equation and equation (8) we have

$$\cos \theta' = \frac{K - 1}{2 + K} \frac{3}{4 \pi n M} \quad (10)$$

where the value of n is given by

$$n = \frac{\rho_1}{m \, 1.66 \times 10^{-24}}$$

Table III gives values of $\cos \theta'$ and of $M \cos \theta'$ for a number of substances in the gaseous state calculated by the foregoing equa-

TABLE III.

Gas.		$\frac{K-1}{K+2}$	$t^\circ \text{ C.}$	$M \cos \theta' \times 10^{25}$	$\cos \theta' \times 10^6$
Hydrogen.....	H ₂	.000088	0	2.6	1.30
Helium.....	He	.0000247	0	.728	.459
Nitrogen.....	N ₂	.000194	0	5.73	.782
Carbon dioxide.....	CO ₂	.000328	0	9.67	.762
Methane.....	CH ₄	.000318	0	9.38	1.27
Hydrochloric acid.....	HCl	.00086	100	34.3	4.52
Carbon disulphide.....	CS ₂	.000796	100	32.1	1.63
Carbon tetrachloride....	CCl ₄	.001013	110	40.8	1.51
Ethyl bromide.....	C ₂ H ₅ Br	.00515	100	207.5	9.31
Benzene.....	C ₆ H ₆	.00090	100	36.1	1.36
Methyl formate.....	C ₂ H ₄ O ₂	.0023	100	92.7	5.93
Methyl acetate.....	C ₂ H ₆ O ₂	.0024	100	96.7	5.48
Ethyl propionate.....	C ₅ H ₁₀ O ₂	.0047	100	189.0	6.00

tion. The values of K were obtained from a table given in the "Handbuch der Electricität und des Magnetismus" by Dr. L. Grätz, and correspond to standard pressure at the temperatures given. The values of M were taken from Table II. It will be seen that in all cases $\cos \theta'$ is a very small fraction, and θ' therefore nearly a right angle. Thus the directive action of an electric field of one electrostatic unit is very small. Evidently an enormous field, of the order 10^6 e.s.u., or 10^8 volts, would be necessary, on account of the disturbing action of molecular collision, to keep the molecular doublets approximately parallel to the lines of electric force. The values of $\cos \theta'$ for different substances are probably strictly comparable only at corresponding states, which

does not apply to the values given in the table. It is evident, however, that they probably would, under ideally comparable conditions, increase with increase in the moment of the molecule, as we might expect. The angle θ' must be besides a function of the nature and frequency of molecular collision, and is thus on the whole a complicated quantity.

We would expect therefore that the more violent the molecular collision the more it would interfere with the doublets tending to set themselves parallel to an electric field. It would follow therefore that the inductivity of a gas kept at constant volume should decrease with increase in temperature, provided no dissociation takes place. This agrees with the facts.

The frequency of molecular collision, which increases with increase of density at constant temperature, should also tend to decrease the value of $\cos \theta'$. On the other hand, the tendency of an atomic doublet to set itself parallel to the electric field will react on the other doublets of the substance, tending to set them in the same direction, which would increase the value of $\cos \theta'$. The effect of one doublet on the other at any instant would of course depend on their distance of separation. The latter effect would increase with increase of density of the substance, and is thus in the opposite direction to the former effect. The relative importance of these two effects will appear on comparing the values of $M \cos \theta'$ for a number of liquids given in Table IV with

TABLE IV.

Liquid.		K.	t° C.	ρ_1	$M \cos \theta' \times 10^{25}$
Benzene.....	C_6H_6	7.316	18	.8808	640.9
Carbon disulphide.....	CS_2	2.626	20	1.2625	126.
Ethyl oxide.....	$C_4H_{10}O$	4.68	0	.7362	481.0
.....	4.30	20	.7135	445.2
.....	3.65	60	.6658	383.2
.....	3.12	100	.6105	334.3
.....	2.66	140	.5385	296.8
.....	2.12	180	.4268	252.6
Hexane.....	C_6H_{12}	1.880	17	.6605	149.3
Octane.....	C_8H_{16}	1.949	17	.7033	200.3
Acetone.....	C_3H_6O	26.6	0	.8126	2360.
Carbon dioxide.....	CO_2	1.60	-5	.930	36.94
Chloroform.....	$CHCl_3$	5.2	18	1.4885	438.4

those given in Table III for a number of gases. It will be seen that the values for the liquid state are greater than those for the gaseous, and the latter effect is therefore more pronounced for this

state than the former. When a substance is approximately in the perfectly gaseous state these effects are nearly equal since the inductivity under these conditions is found to be approximately proportional to the density of the gas.

An increase in temperature increases the violence of molecular collision and hence the angular velocity of molecular rotation, which would necessarily be attended by a change in the geometrical configuration of the atoms of each molecule. We would therefore expect that the specific heat of a gas should be a function of the electrical moments of the atoms of a molecule. This is found to be the case. Table V gives the specific heat c_v per gram mole-

TABLE V.

Gas.		c_v	c_i	$\frac{\log_{10} c_i}{\Sigma a_{\omega}^{1/2}}$	$\frac{\log_{10} c_i}{\Sigma N^{2/3}}$
Carbon disulphide.....	CS ₂	8.01	5.07	475	441
Chloroform.....	CHCl ₃	14.05	11.11	468	433
Ethyl bromide.....	C ₂ H ₅ Br	12.72	9.78	452	442
Acetone.....	C ₃ H ₆ O	15.30	12.36	536	548
Benzene.....	C ₆ H ₆	15.48	12.54	410	425
Ethyl acetate.....	C ₄ H ₈ O ₂	21.00	18.06	424	430
Ether.....	C ₄ H ₁₀ O	25.50	22.56	486	497

cule of a number of substances in the gaseous state at constant volume, and the values of $c_v - \frac{3}{2} R = c_i$ where $\frac{3}{2} R$ is the part of the specific heat due to the change in kinetic energy of motion of translation of the molecules. The internal specific heat c_i represents the change in the internal molecular energy per degree change in temperature. It is found that

$$\log_{10} c_i = h_1 \Sigma N^{2/3} = h_2 \Sigma a_{\omega}^{1/2} \quad (11)$$

where a_{ω} denotes the atomic weight of an atom, and h_1 and h_2 are constants, as is shown by the values obtained from this equation and given in the table.

The values of c_v used refer to the temperature 0° C. and were taken from "Winckelmann's Handbuch der Physik," 2nd ed. It is very probable, however, that these quantities are comparable only at corresponding temperatures, in parallel with so many other properties of substances. We would then have

$$\log_{10} c_i = \phi_1 \left(\frac{T}{T_c} \right) \cdot \Sigma N^{2/3} \quad (12)$$

where T_c denotes the absolute critical temperature, and $\phi_1 \left(\frac{T}{T_c} \right)$ a function of T/T_c .

The method of obtaining the absolute value of the electrical moment of an atom developed in this paper could not very well be simpler or more straightforward. Attempts have previously been made by Jona, Frivolds, and Debye¹² to obtain a value of this quantity from data on electric inductivity and cohesion. In order to obtain formulas that can be applied to the facts it was necessary to introduce assumptions which introduced other quantities besides the above. These formulas would therefore naturally not be so trustworthy as the one developed in this paper. The values obtained for the electrical moment of a few molecules are, however, it is interesting to note, of the same order of magnitude as those given by equation (3).

Comparison of Resistance Changes in Longitudinal and Transverse Magnetic Fields. W. H. SANDERS and A. P. CARMAN. (*Phys. Rev.*, Feb., 1923.)—Wire of copper, silver, manganin and also Advance wire were placed in magnetic fields of strengths from 4 to 16 kilogausses, so that the magnetic lines of force were in one position perpendicular to the wires and in the other parallel to them. In both positions the copper and the silver wires showed an increase in the electrical resistance, while in both positions the two alloy wires showed a decrease. For all wires in both positions the change in the resistance increased with increasing field strength. The change in resistance was greater when the wire was transverse to the field than when it was parallel, though in the case of the Advance wire the difference was but slight. This wire showed the least change of resistance and copper the greatest. All changes measured were small, the largest, the change in copper wire, transverse to the field of 16 kilogausses, being 645 ten-millionths of the resistance in the absence of a field.
G. F. S.

Chlorine Isotopes in Apatite. MARGOT DORENFELDT, of the University of Christiania (*Jour. Am. Chem. Soc.*, 1923, 45, 1577–1579), has determined the specific gravity and sodium chloride content of saturated aqueous solutions of ordinary sodium chloride and of sodium chloride whose chlorine content was derived from the mineral apatite mined in Bamle. Her results show that the isotopes of chlorine occur in the apatite in the same proportion as an ordinary sodium chloride.
J. S. H.

¹² *Phys. Zeit.*, 20, p. 14; 22, p. 603; 21, p. 178.

Action of Potassium Carbonate on Lead Glass. H. DROOP RICHMOND (*Analyst*, 1923, 48, 260-262) has shown by experiment that potassium carbonate is sufficiently hygroscopic to attack the glass of the bottle in which it is stored, especially if it become moist. A thin film of a very concentrated solution of potassium carbonate forms on the surface of the crystals. If the glass contain arsenic and lead, the film in contact with the glass dissolves these elements as potassium arsenite and plumbate. When the contents of the bottle are disturbed, the contaminated crystals are mixed with the bulk of the carbonate. A bottle had been used continuously for at least nine years as a container for potassium carbonate. The loose salt, which could be removed from the bottle by ordinary shaking, contained seven parts of arsenic and between 200 and 300 parts of lead per million. The salt, which adhered to the glass, was collected by scraping, and found to contain twelve parts of arsenic and 500 parts of lead per million. The bottle was washed; and its inner surface was found to be corroded. The glass of the bottle was analyzed, and yielded 0.34 per cent. arsenious oxide and 31.1 per cent. lead oxide. The salt was a pure potassium carbonate, containing merely traces of chloride, sulphate, phosphate, iron, alumina, and ammonia; it yielded a turbid solution, the insoluble matter consisting largely of silica; the lead and arsenic had been dissolved from the glass.

J. S. H.

Removal of Small Amounts of Carbon Monoxide from Gases.—In the arts, traces of carbon monoxide frequently have to be removed from gases, for instance, in order to prevent the poisoning of a catalyst. ROBERT E. WILSON, C. A. HASSLACHER, and E. MASTERSON, of the Massachusetts Institute of Technology (*Ind. Eng. Chem.*, 1923, 15, 698-701), find that small amounts (2 per cent.) of carbon monoxide are removed from nitrogen more efficiently by soda lime of high sodium hydroxide content than by soda lime of low sodium hydroxide content or by lime alone. Using soda lime of high sodium hydroxide content, the carbon monoxide is practically completely removed at a temperature of approximately 400° C. Small amounts of water increase the efficiency of the reaction, but are not essential. The reaction has as its products sodium carbonate and hydrogen.

J. S. H.

New Applications of the Phenol Resins.—According to L. V. REDMAN (*Ind. Eng. Chem.*, 1923, 15, 677) measuring cylinders and conductivity cells for hydrofluoric acid are made from pure synthetic phenol resins. Laminated products made from these resins are used in the manufacture of barrels and conveyor chains for cyanide plating, valves and their discs in pumps for deep oil wells or for handling corrosive animal by-products, silent gears, buttons, door knobs, mechanical parts on typewriters and adding machines, insulators in the automatic telephone, and parts for radio apparatus.

J. S. H.

THE SHORT-WAVE RADIATION FROM TUNGSTEN FILAMENTS.* †

BY

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VI. ANALYSIS OF THEORETICAL AND EXPERIMENTAL DATA ON PHOTOGRAPHIC ACTINICITIES OF RADIATIONS FROM A TUNGSTEN FILAMENT AT VARIOUS TEMPERATURES AFTER TRAVERSING VARIOUS BULB-GLASSES.

The purpose of this part of the investigation was to study analytically the influences of the spectral sensitivity of the emulsion, the spectral transmission of the bulb-glass and the temperature of the tungsten filament upon the resultant radiations and their effects upon vision and the photographic emulsion.

When given the spectral intensity J_λ of radiant flux in ergs per sq. cm. per second from incandescent tungsten at temperature T , the spectral transmission t_λ of the bulb-glass, the visibility V_λ of the normal eye, then the luminous intensity I in candles per square centimetre can be computed by integrating the product of flux density, transmission, visibility and the element of wave-length $d\lambda$, or

$$I = \frac{1}{\pi M} \int_0^\infty J_\lambda t_\lambda V_\lambda d\lambda \quad (1)$$

where M , the mechanical equivalent of light of maximum visibility, is 15,000 ergs per second per lumen.

By using the definitions and symbols given in Part II, it may be easily shown that when the sensitivity, S , or $\frac{I}{E}$, of the emulsion at standard wave-length 436 m μ , the spectral-sensitivity S_λ for any wave-length λ , the spectral transmission t_λ of the interposed medium and the spectral intensity J_λ of the radiant flux are

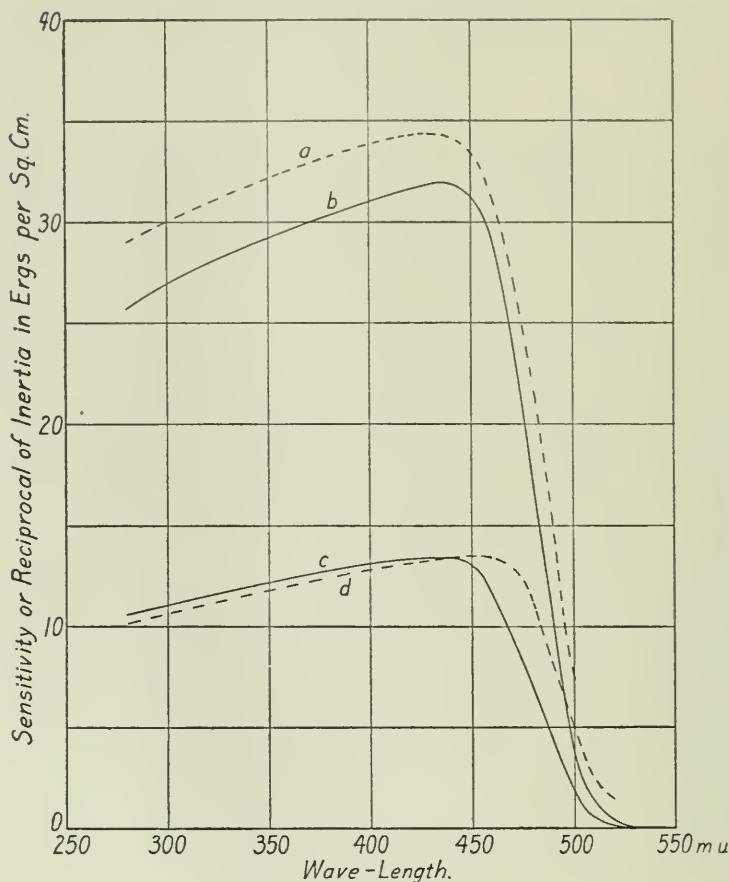
* Communicated by the Director of the Laboratory.

† Concluded from JOUR. FRANK. INST., 196, No. 3, Sept., 1923, p. 373.

known, then the combined efficiency of the transmitting medium and the photographic emulsion is

$$\rho = \frac{1}{S} \frac{\int_0^\infty t_\lambda S_\lambda J_\lambda d\lambda}{\int_0^\infty J_\lambda d\lambda}. \quad (2)$$

FIG. 8.



Spectral sensitivity curves of four photographic emulsions: (a) Orthonon; (b) Seed's 26; (c) Seed's 23; (d) W. and W. panchromatic.

Similarly, when ρ and S are known the actinicity may be shown to be

$$A = \frac{1}{E_r} = \frac{\rho}{E} = \rho S \quad (3)$$

or when the spectral transmission of the medium, spectral sensitivity of the emulsion and the spectral flux density are known, the actinicity of the radiation may be shown to be

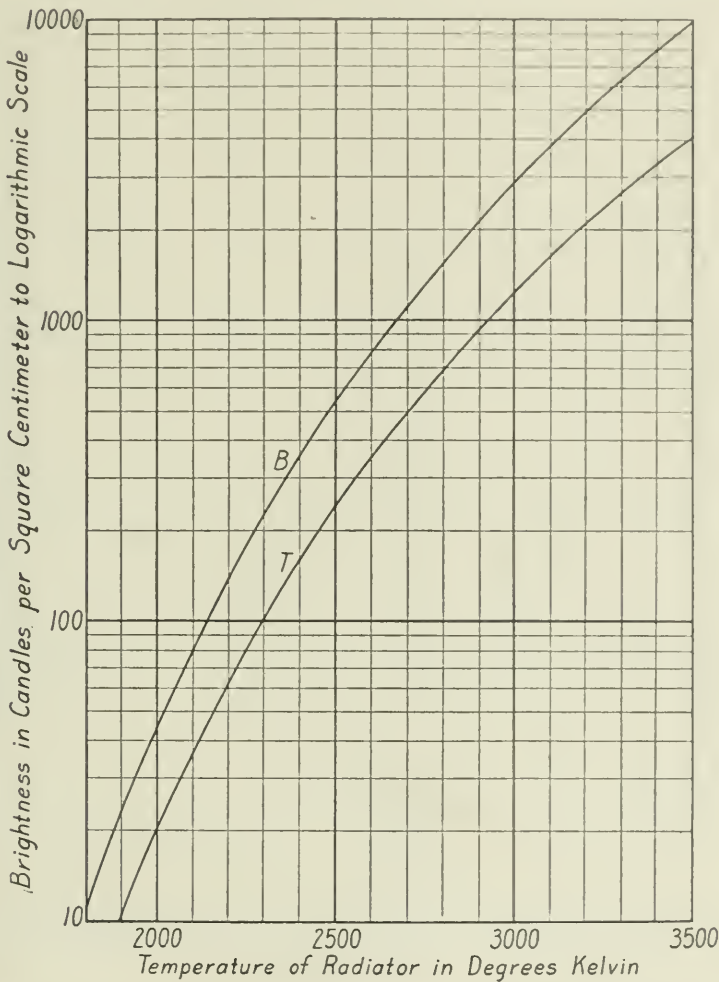
$$A = \frac{\int_0^\infty t_\lambda S_\lambda J_\lambda d\lambda}{\int_0^\infty J_\lambda d\lambda} \quad (4)$$

Also when the spectral transmission of medium, spectral sensitivity of the emulsion and spectral flux density of radiation are known, the photographic effectiveness Q of the radiation may be proved to be

$$Q = \frac{I}{t} = \int_0^\infty t_\lambda S_\lambda J_\lambda d\lambda \tag{5}$$

or when the sensitivity S of the emulsion at wave-length $436\text{ m}\mu$,

FIG. 9.



Temperature-brightness curves, (B) for a "black-body" radiator and (T) for tungsten.

the combined efficiency of medium and radiation ρ , and the spectral flux density are known, then the photographic effectiveness Q may be proved to be

$$Q = \frac{I}{t} = \rho S \int_0^\infty J_\lambda d\lambda \tag{6}$$

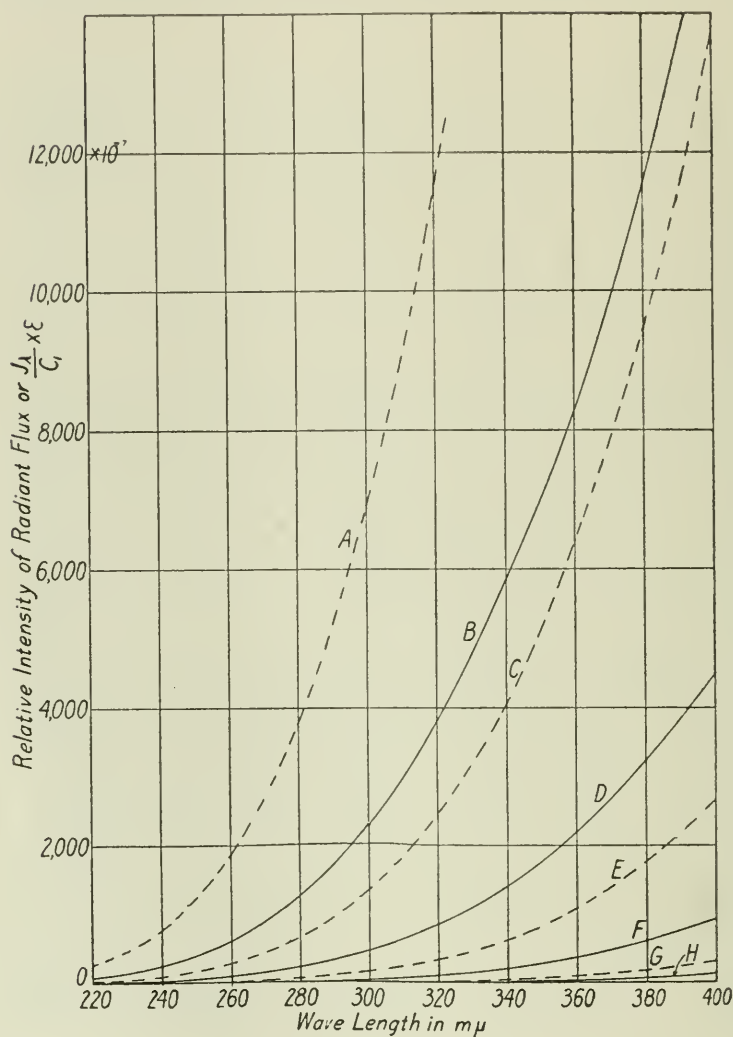
Wien's equation for the intensity of radiant flux from a

black-body at a temperature of T° Kelvin and wave-length λ in μ is

$$J_\lambda = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} \quad (7)$$

where e is the base of the natural system of logarithms and C_1

FIG. 10.



Intensity of radiant flux from tungsten and a "black-body" radiator at various temperatures. Black-body at (A) 3600° K., (C) 3200° K., (E) 2800° K., (G) 2400° K. Tungsten at (B) 3495° K., (D) 3115° K., (F) 2735° K., (H) 2350° K.

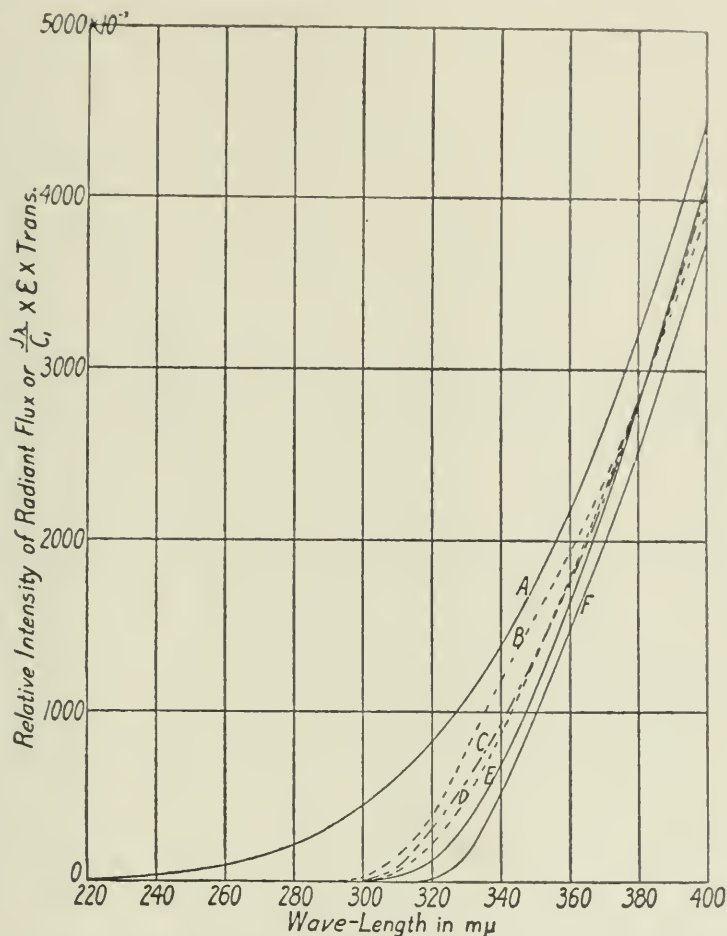
and C_2 are constants. From data presented by Forsythe,⁹ Coblantz¹⁰ and others, the value of C_2 is taken as $14,350\mu$ degrees and C_1 as 3.72×10^{-12} watts per square centimetre or as 3.72×10^{-5} ergs per second per square centimetre.

The intensity of radiant flux of wave-length λ for a non-black-body at temperature T is given by the equation:

$$J_{\lambda} = \varepsilon_{\lambda} C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} \quad (8)$$

where ε_{λ} is a factor defined as the emissivity which is always less than unity. Combining the data of Worthing¹¹ and of Hulburt¹²

FIG. 11



Spectral intensity of radiant flux from tungsten at 3115° K. (color temperature 3200° K.) through quartz and various lamp-bulb glasses. Through (A) quartz, (B) soda-lime glass, (C) Mazda C-3 photographic glass, (D) soda-lead glass, (E) boro-silicate hard glass, (F) Mazda C-2 daylight glass.

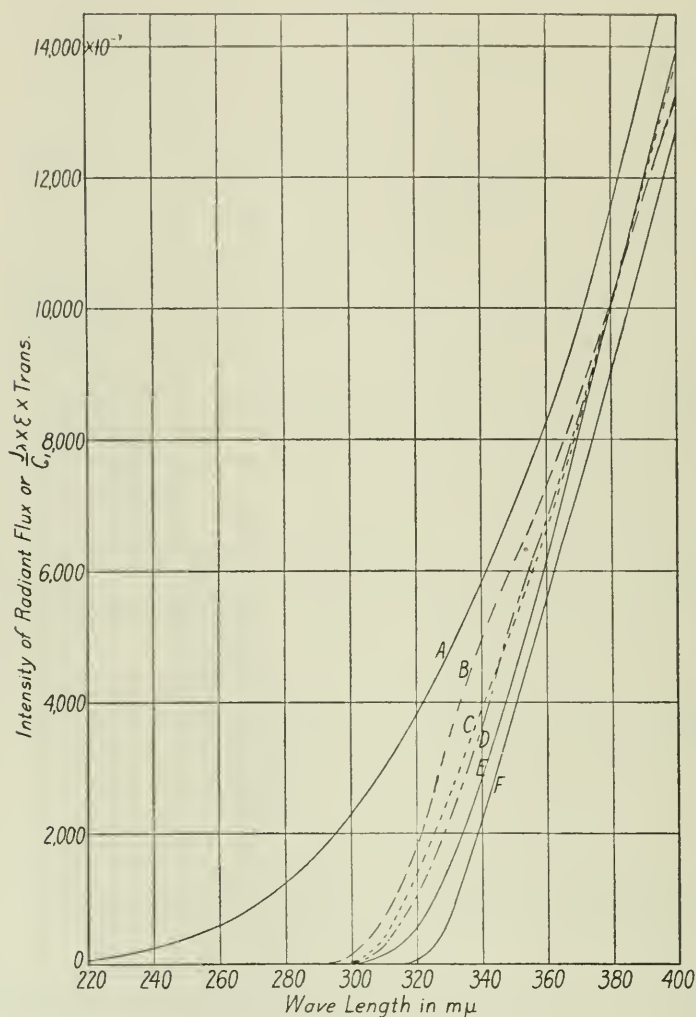
we obtain an empirical equation for emissivity of tungsten for λ in μ and temperature T on the Kelvin scale. This empirical equation is

$$\varepsilon_{\lambda} = \frac{0.45}{\lambda^{0.2}} - \frac{25}{10^6} T. \quad (9)$$

Values of emissivity computed from this equation are in good agreement with Worthing's data, and with Hulburt's, excepting

in the neighborhood of $580\text{ m}\mu$. The spectral region covered by their experiments was from 340 to $665\text{ m}\mu$. Computed values of emissivities for various wave-lengths are presented in Table III. If this equation for emissivity should be combined with Wien's equation for a black-body, the resulting equation would *probably*

FIG. 12.



Spectral intensity of radiant flux from tungsten at 3495°K. (color temperature 3600°K.) through quartz and through various lamp-bulb glasses. Through (A) quartz, (B) soda-lime glass, (C) Mazda C-3 photographic glass, (D) soda-lead glass, (E) boro-silicate hard glass, (F) Mazda C-2 daylight glass.

give substantially correct values for the energy distribution for tungsten in the visible and near ultra-violet regions of the spectrum. The equation would then be as follows:

$$J_\lambda = \left(\frac{0.45}{\lambda^{0.2}} - \frac{25T}{10^6} \right) C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} \quad (10)$$

The emissivity of a black-body by definition being equal to unity, if the temperature of a black-body is raised to T_c so that the color of the black-body radiation is the same as the color of

FIG. 13.



Curves illustrating various factors entering into visual and photographic effects, and the resultant effects of various factors. (a) Radiant flux from tungsten at 2350° K.; (b) relative visibility curve of a normal eye; (c) relative luminosity of radiant flux from tungsten at 2350°—product of curves (a) and (b); (d) spectral transmission curve of Mazda C-3 photographic glass; (e) relative luminosity of radiant flux from tungsten at 2350° K., through Mazda C-3 photographic glass—product of curves (a), (b), (c) and (d); (f) spectral sensitivity curve of Seed's 23 emulsion; (g) and (h), photographic effectiveness of radiant flux from tungsten at 2350° K. through quartz and through C-3 photographic glass, respectively.

tungsten radiation when at a temperature T or, if the temperature of the black-body T_c is such that the ratios of brightnesses of the tungsten and black-body are the same for two wave-lengths λ_1 and λ_2 , when the true temperature of the tungsten is T , then the

tungsten is said to have a color temperature T_c . Values of color temperatures and true temperatures for tungsten are given in Table IV. These are obtained from data by Worthing,¹³ who has also deduced a so-called pseudo-emissive power for tungsten. This may be defined as the ratio of brightness of tungsten at its true temperature T to the brightness of a black-body at temperature T_c , the so-called color temperature, at which the color

TABLE III.

Table of emissivities of incandescent tungsten for various wave-lengths and temperatures computed from the empirical equation (9).

Computed Emissivities.					
Wave-length m μ .	1500° K.	2000° K.	2500° K.	3000° K.	3500° K.
340	0.521	0.508	0.496	0.484	0.471
380	.509	.496	.485	.471	.458
420	.498	.485	.473	.460	.448
460	.488	.475	.463	.450	.438
467*	.484	.474	.463	.451
500	.479	.467	.454	.442	.429
540	.471	.459	.446	.434	.421
580	.464	.452	.439	.427	.414
620	.458	.445	.433	.420	.408
660	.451	.439	.426	.414	.401
665*	.448	.444	.429	.416	.400

*Values taken from Worthing's data.

of tungsten radiation matches that of black-body radiation. Worthing's values of pseudo-emissive powers are also given in Table IV. Brightnesses of a black-body and tungsten given in this table are shown in Fig. 9.

The pseudo-emissive power of tungsten may be computed from the equation

$$\epsilon = 0.42 - \frac{25}{10^6} T \quad (11)$$

where ϵ is the pseudo-emissive power and T is the true temperature of the tungsten in degrees Kelvin. This equation has been derived from the values of pseudo-emissive power given by Worthing.¹³

Approximate values of the intensity of radiant flux from incandescent tungsten at true temperature T and color tempera-

ture T_c for the visible spectrum and *probably* for the near ultra-violet, may be computed by use of the equation

$$J_\lambda = \varepsilon C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T_c}}$$

(12)

where values of ε , the pseudo-emissive power, are obtained from Table IV or calculated as above. Substituting ε from equation (11), we have

$$J_\lambda = \left(0.42 - \frac{25}{10^6} T \right) C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T_c}}$$

(13)

Values of intensity of radiant flux for a black-body at various wave-lengths and temperatures have been computed from Wien's

TABLE IV.

Table showing the brightness of a black-body and of incandescent tungsten at various true temperatures, these data being computed by use of values of the brightness of a black-body obtained from data by Forsythe⁹ and pseudo-emissive powers and color temperatures for tungsten as given by Worthing.¹³

Tungsten.		Pseudo-emissive power of tungsten for wave-lengths .467 μ and .665 μ	Brightness in candles per sq. cm.	
True Temp. T	Color Temp. T_c		Of black-body at temp. T_c	Of tungsten at temp. T
1200° K.	1211° K.	0.391	0.0158	0.0062
1600	1620	.380	2.57	0.98
2000	2032	.370	54.	20.
2400	2448	.360	437.	157.
2800	2868	.350	1,945.	680.
3200	3292	.340	6,095.	2070.
3600	3720	.329	15,100.	4970.
3675	3800	.328	17,700.	5805.

equation (7) and are given in Table V and plotted in Fig. 10. Values for incandescent tungsten have been computed by use of equation (12) and these are also plotted in Fig. 10. By multiplying the values of radiant flux from tungsten by the transmission-factors of various bulb-glasses 0.8 mm. thick, values of the flux transmitted by the glasses have been obtained for filament temperatures of 3115 and 3495° K., the former being near the practical operating limit of tungsten, and the latter 180° below its melting point. The values are shown graphically in Figs. 11 and 12.

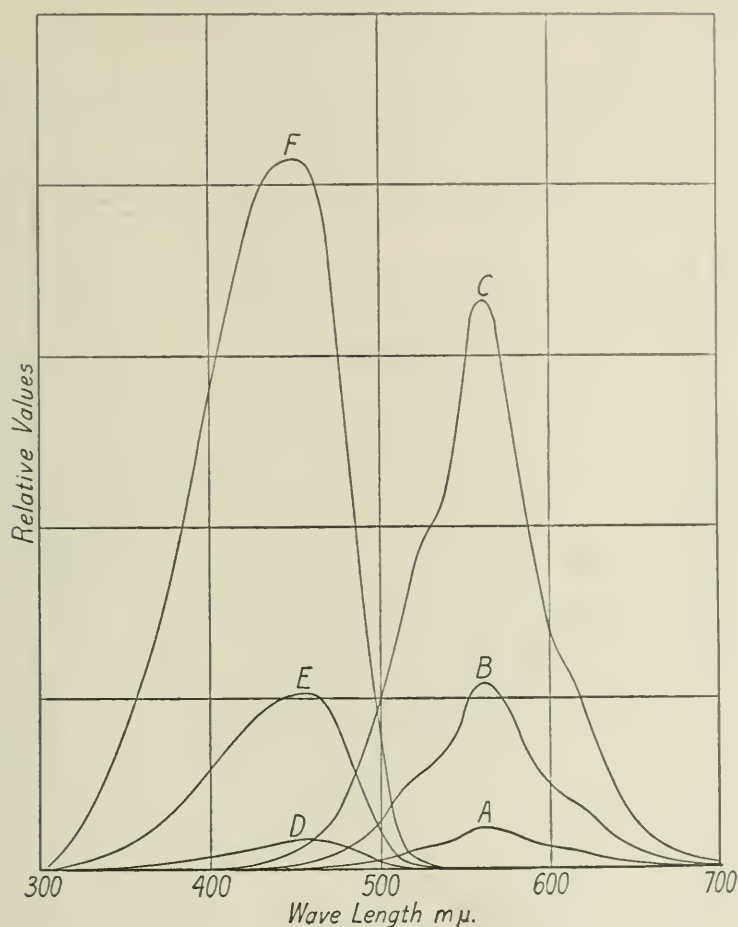
In Table VI are given authoritative values of relative visibility for the average eye. A plot of these data is given on Fig. 13, curve *b*.

TABLE V.
Relative Intensity of Radiant Flux for a Black-body Radiator Calculated from Wien's Equation.

Wave-length in μ .	Relative intensity of radiant flux or J_{λ}/c_1 .				
	2000° K.	2400° K.	2800° K.	3200° K.	3600° K.
0.22		0.0305×10^{-7}	1.865×10^{-7}	27.25×10^{-7}	262.4×10^{-7}
.24		.140	6.68	96.4	768.8
.26		.866	23.13	271.9	1,848.
.28			65.33	643.9	3,815.
.30		3.09	156.75	1,325.5	6,980.
.32		9.09	331.8	2,445.	11,600.
.34		22.87	625.5	4,117.5	17,820.
.36		50.71	1,089.5	6,436.	25,100.
.38		101.28	1,753.	9,460.	35,101.
.40		185.1	2,662.8	13,207.	46,100.
.44		314.7	5,298.	22,720.	70,510.
.46		760.6	7,041.	26,300.	83,760.
.48		1,099.5	9,053.	34,388.	97,100.
.52		1,528.	13,792.	47,280.	123,250.
.56		2,669.	19,251.	60,430.	147,150.
.58		4,190.	22,200.	67,800.	157,800.
.60		5,079.	25,105.	72,990.	167,520.
.62		6,046.	27,900.	79,000.	176,180.
.64		7,077.	30,982.	84,350.	183,320.
.66		8,162.	33,650.	88,500.	190,240.
.68		9,285.	36,600.	92,500.	195,730.
.70		10,440.	39,346.	96,005.	200,220.
.72		11,610.	39,800.	99,600.	203,680.
.74		12,790.	45,150.	102,700.	206,270.
.76		13,960.	48,000.	105,600.	208,280.
		15,110.			

Using equation (1), relative values of luminosity of tungsten through air and through Mazda C-3 photographic glass have been computed for a filament temperature of 2350° K., and plotted spectrally in curves *c* and *e*, respectively, in Fig. 13. In a similar

FIG. 14.



Relative luminosity curves for radiant flux from tungsten at (A) 2350° K., (B) 2735° K. and (C) 3115° K. Relative photographic effectiveness curves for radiant flux from tungsten at (D) 2350° K., (E) 2735° K., and (F) 3115° K.

manner, using equation (5), the relative photographic effectiveness on a Seed's 23 plate has been computed for the radiations from tungsten at the same temperature of 2350° K. for the same media, and are plotted spectrally in curves *g* and *h* on Fig. 13. It may be noted here that actinivities for Seed's 26 and 23 plates computed by this method are in close agreement with the observed values.

In Fig. 14 to the right are shown spectrally the relative luminosity curves for the radiations of tungsten, at three tem-

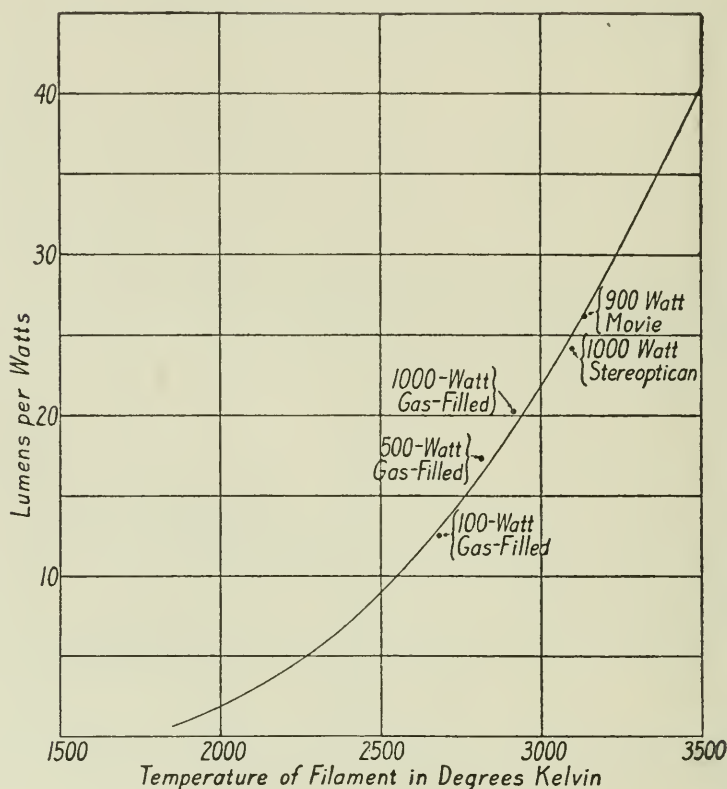
peratures, through Mazda C-3 photographic bulb-glass. Similarly, spectral curves of photographic effectiveness for a Seed's 23 plate, under the same conditions, are shown to the left in Fig. 14.

The brightness B of a black-body at any temperature T may be obtained by evaluation of the integral.

$$B = \frac{1}{\pi M} \int_0^\infty J_{\lambda T} V_\lambda d\lambda \quad (14)$$

where M is the mechanical equivalent of light of maximum visi-

FIG. 15.

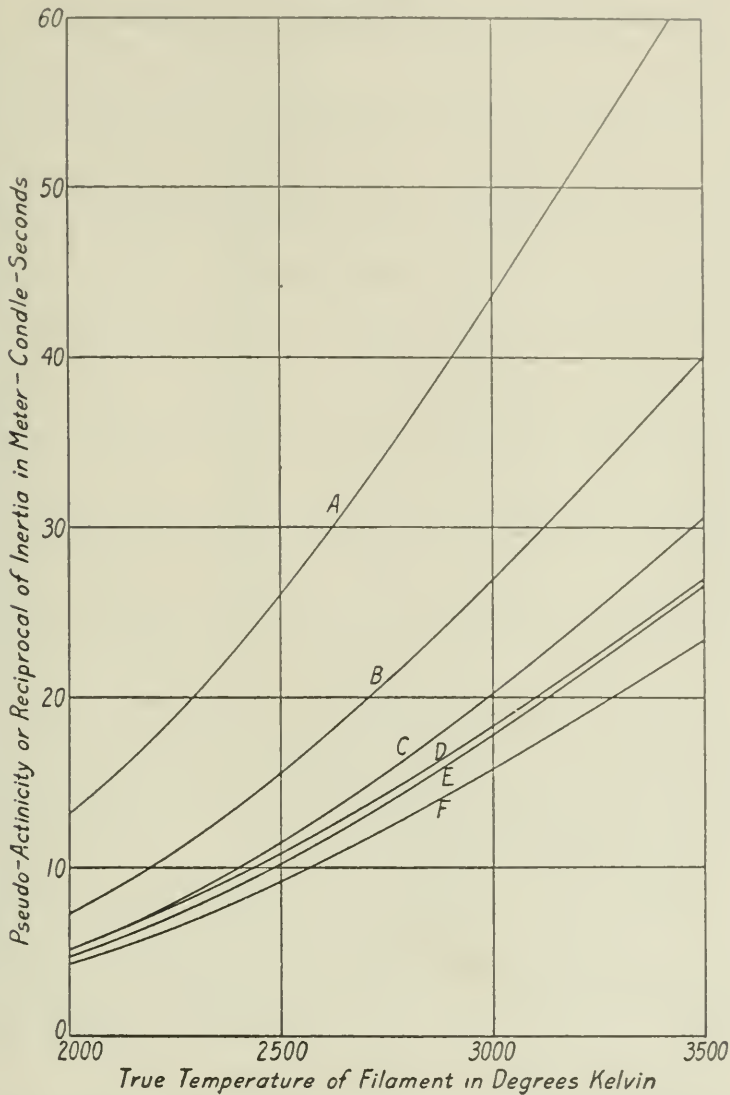


Approximate luminous efficiency (lumens per watt) of gas-filled tungsten lamps at various temperatures.

bility, whose accepted value is .00150 watt per lumen, and V_λ is the relative visibility of radiation as given in Table VI. The brightness of tungsten for temperature T may be obtained by multiplying the brightness of the black-body at the color temperature of tungsten, T_c , by the pseudo-emissive power of tungsten as given in Table IV. Values of brightness for a black-body and tungsten, obtained in the manner described, are given in Table IV and plotted in Fig. 9.

In Table VII are given the brightness and the watts dissipated per square centimetre, and the luminous efficiency of a tungsten radiator at various temperatures in a gas-filled bulb. It is evident

FIG. 16.

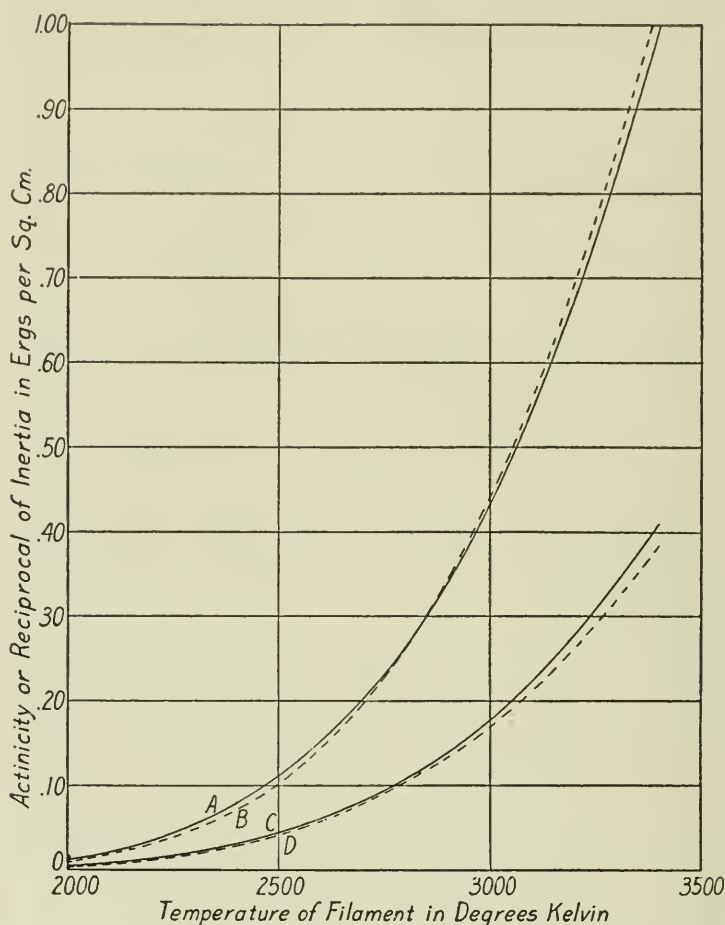


Pseudo-actinic (1 ÷ inertia in metre-candle-seconds) of radiant flux from tungsten as effective on Seed's 26 plates, illumination being measured at plate position with glass interposed. Interposed media: (A) C-3 photographic glass; (B) C-2 daylight; (C) quartz; (D) soda-lime; (E) soda-lead; (F) boro-silicate hard glass.

that watts dissipated per square centimetre and the luminous efficiency may vary somewhat from lamp to lamp, depending upon its size, the type and pressure of gas, etc.; however, these values for any particular lamp would probably not depart very greatly from the relative values given.

Data on Commercial Lamps.—From published¹⁴ and unpublished work by Hyde and Forsythe, data pertaining to certain representative types of lamps have been obtained. They are given

FIG. 17.



Actinicity ($1 \div$ inertia in ergs) of radiant energy from tungsten through quartz, as effective on: (A) Seed's 26, (B) orthonon, (C) Seed's 23, and (D) panchromatic emulsion.

in Table VIII, in which the symbols have the following meanings:

lpw = lumens per watt.

T_c = color temperature (Kelvin) of filament, *i.e.*, the temperature of a black-body which gives light of the same color as that from the lamp considered.

T_m = maximum temperature (Kelvin) of any part of filament.

T_a = approximate *average* true temperature (Kelvin) of the filament.

B = approximate average brightness of filament in candles per square centimetre.

It is of considerable importance to know the relative actinicities of radiations from various typical lamps, considered on the basis

TABLE VI.

Table of the relative visibility of radiation for the average eye, as adopted by the American Engineering Standards Committee.

Wave-length in mμ.	Visibility relative to that at 556 mμ.	Wave-length in mμ.	Visibility relative to that at 556 mμ.
400	0.0004	580	0.870
410	.0012	590	.757
420	.0040	600	.631
430	.0116	610	.503
440	.023	620	.380
450	.038	630	.262
460	.060	640	.170
470	.091	650	.103
480	.139	660	.059
490	.208	670	.030
500	.323	680	.016
510	.484	690	.0081
520	.670	700	.0041
530	.836	710	.0021
540	.942	720	.0010
550	.993	730	.00052
556	1.000	740	.00025
560	.996	750	.00012
570	.952	760	.00006

TABLE VII.

Table showing approximately the variation of brightness, watts and lumens per watt of a tungsten filament at various temperatures (Kelvin) in a gas-filled bulb.

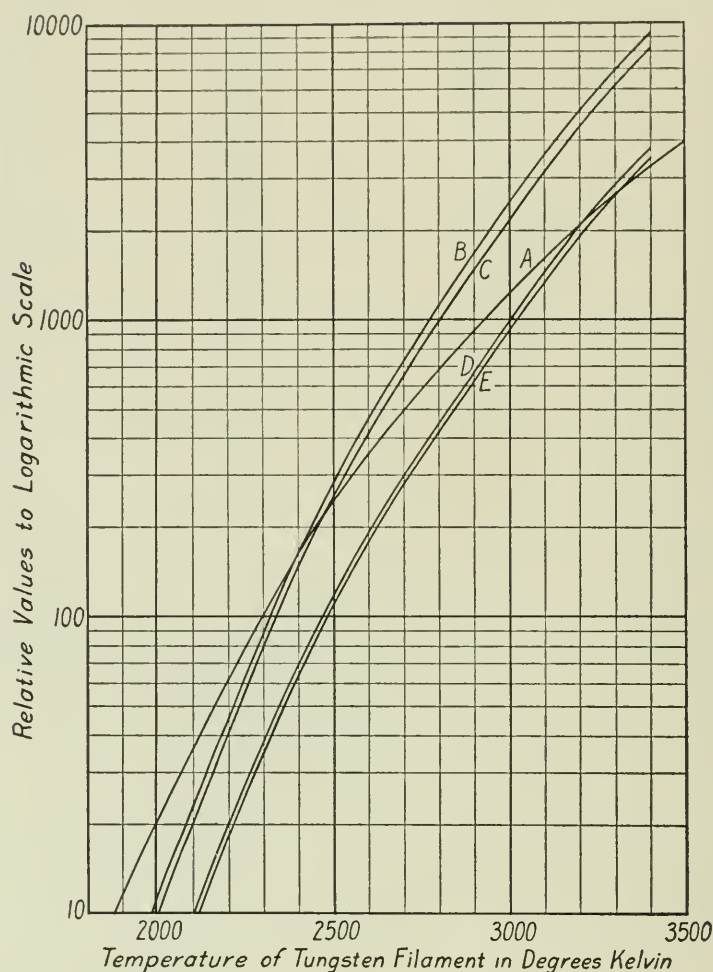
True temp. of tungsten filament in degrees Kelvin.	Brightness of tungsten.		Watts dissipated per sq. cm. of radiator in gas-filled bulb.		Luminous efficiency.	
	Candles per sq. cm.	Relative to brightness at 3000° K.	Per sq. cm.	Relative to watts at 3000° K.	Lumens per watt.	Relative to efficiency at 3000° K.
2000° K.	20.	1.7	35	20.2	1.83	8.3
2200	61.5	5.1	47	27.2	4.1	18.7
2400	157.	13.0	71	41.2	7.1	32.3
2600	352.	29.1	98	56.8	11.3	51.2
2800	680.	56.2	131	76.0	16.1	73.4
3000	1210.	100.	173	100.	22.0	100.
3200	2070.	171.	226	131.	28.7	130.5
3400	3300.	273.	284	164.5	36.5	165.7
3500	4080.	337.	317	183.5	40.5	183.8

of equal watts input. From the tables already given and from other data relative actinicities for the various lamps have been computed. For convenience these actinicities are given relatively

to that for a 1000-watt Mazda C-3 photographic lamp operating at an average temperature of 3000° K., which is approximately its normal operating temperature. These data are given in Table IX.

In Table I, Part III, have been given pseudo-actinicities of the radiations from incandescent tungsten, as measured by four types

FIG. 18.



(A) Temperature-brightness curve for tungsten. Photographic effectiveness ($1 \div$ inertia in seconds only) of radiant energy from tungsten through quartz, as measured by (B) Seed's 26, (D) Seed's 23 emulsion. Through soda-lead glass, as measured by (C) Seed's 26, (E) Seed's 23 emulsion.

of photographic emulsions, with various lamp-bulb glasses interposed. In those data the illumination (metre-candles) was measured without the glass interposed, and a deduction of 8 per cent. for reflection by the glass specimen was made. Since the illumination would normally be measured after the radiations have passed through the glass bulb, the data in Table I have been

reduced to this basis, and are presented in Table X. These data for a Seed's 26 plate are also shown in Fig. 16.

Actinicies, or the reciprocals of inertias in ergs per square centimetre of emulsion for radiations from tungsten at various temperatures, are given in Table XI for quartz and for soda-lead

TABLE VIII.
Data Pertaining to Representative Tungsten Lamps.

Type of lamp.	<i>lpw.</i>	T_c	T_m	T_a	<i>B</i>
40-watt vacuum....	10	2500° K.	2410° K.
100-watt gas-filled..	12.6	2740	2745	2680° K.	455
500-watt gas-filled..	17.4	2880	2835	2810	695
1000-watt gas-filled.	20.3	2985	3010	2910	930
1000-watt stereopti- can.....	24.2	3175	3185	3095	1575
900-watt movie.....	26.2	3220	3290	3135	1750

TABLE IX.
Table of Relative Actinicies of the Radiations from Various Typical Gas-filled Lamps.

Lamp.	Type of bulb-glass.	Approx. temp.	Relative actinicies of radiations.			
			Seed's 26.	Seed's 23.	Orthonon.	Panc.
100-watt.....	Soda-lime	2680° K.	52	44	49	68
500-watt.....	Soda-lead	2810	70.5	60	69.5	92
500-watt C-2...	Daylight	2810	69	58	65	78
1000-watt.....	Soda-lead	2910	87.5	75	86.5	116
1000-watt stere- optican.....	Boro-silicate	3095	130	107	119	149
1000-watt C-3..	Photographic	3000	100	100	100	100
900-watt (movie).....	Boro-silicate	3135	143	117	130	163

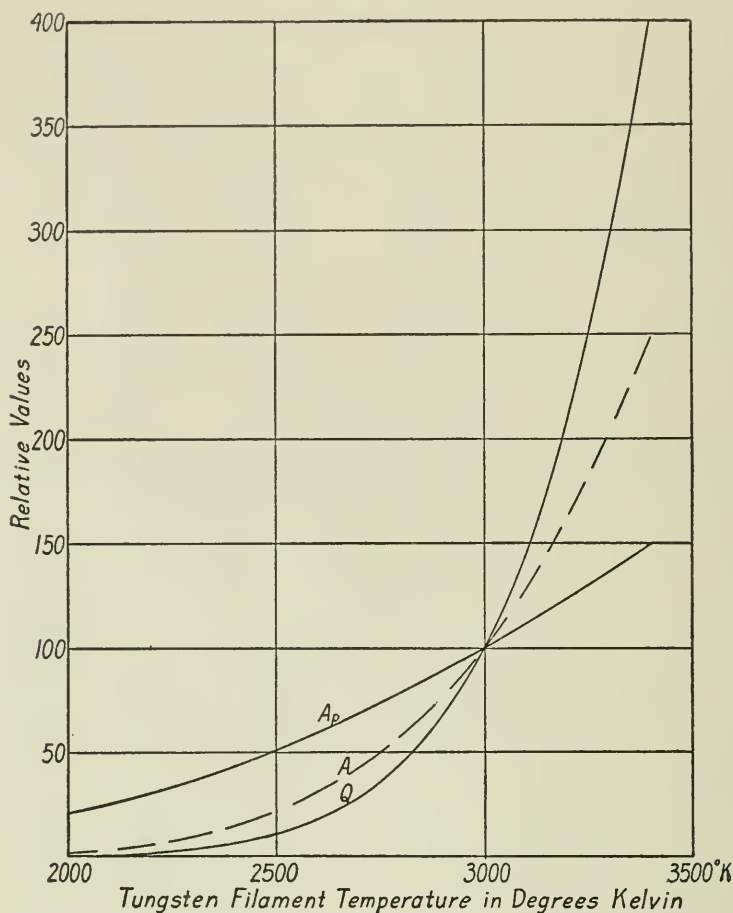
glass. The results for the other clear glasses do not differ materially from these two, but may be easily deduced by anyone interested in them. The actinicies for quartz are also shown in Fig. 17.

The combined effects of increase in intensity and actinicity of the radiant flux with increasing temperature of the tungsten filament are shown by the values of photographic effectiveness (reciprocal of inertia in seconds *only*) tabulated in Table XII. As in Table XI, the data are given for quartz and soda-lead glass

only, but others may be deduced in the manner described. The data for the Seed's emulsions are shown in Fig. 18.

In Table XIII are shown relative values of *pseudo-actinic*ity, *actinic*ity and *photographic effectiveness* of the radiations from incandescent tungsten at various temperatures. In other words,

FIG. 19.



Variation of actinic (*A*), pseudo-actinic (*A_p*), and photographic effectiveness (*Q*) with temperature of the tungsten radiator (Seed's 26 emulsion).

these are the relative reciprocals of inertias in seconds for conditions of constant metre-candles, constant watts and for the total radiant energy, respectively, in terms of their values at a filament temperature of 3000° K. The data for the soda-lead glass and Seed's 26 emulsion are also shown graphically in Fig. 19. These data plotted against lumens per watt are shown in Fig. 20.

In Table XIV and Fig. 21 are given data regarding the rate of change of photographic effectiveness, pseudo-actinic, and acti-

nicity of the radiations from tungsten for definite temperature and voltage changes. The data are given for soda-lead glass and

TABLE X.

Table of pseudo-actinivities of radiations from tungsten at various temperatures through various bulb-glasses as measured by the four types of emulsions, the metre-candles being measured at the plate with glasses interposed. This table is derived from Table I, Part II, by dividing by one minus the absorption of the bulb-glass specimens.

Type of glass in lamp-bulb.	Pseudo-actinicity or reciprocal of inertias in metre-candle-seconds, the illumination being measured at the plate.							
	2000° K.	2200	2400	2600	2800	3000	3200	3400° K.
<i>Seed's 26 Plate</i>								
Quartz.....	5.2	7.4	10.0	13.0	16.4	20.1	24.2	28.4
Soda-lead.....	4.7	6.6	9.0	11.7	14.5	17.7	21.1	24.7
Soda-lime.....	5.2	7.2	9.6	12.2	15.1	18.2	21.6	25.2
Boro-silicate.....	4.4	6.	8.1	10.4	13.0	15.8	18.8	21.9
C-2 daylight*.....	7.2	10.2	13.7	17.7	22.	26.9	32.	37.4
C-3 photographic*...	12.6	17.4	23.4	30.3	37.7	46.0	54.6	63.5
<i>Seed's 23 Plate</i>								
Quartz.....	2.4	3.2	4.2	5.4	6.7	8.1	9.7	11.3
Soda-lead.....	2.2	3.0	4.0	5.1	6.3	7.7	9.1	10.6
Soda-lime.....	2.3	3.1	4.1	5.2	6.5	7.8	9.4	10.9
Boro-silicate.....	2.1	2.9	3.8	4.9	6.1	7.4	8.9	10.4
C-2 daylight.....	3.1	4.3	5.9	7.5	9.5	11.5	13.8	16.2
C-3 photographic....	5.7	8.0	11.1	14.3	18.0	22.0	26.3	30.9
<i>Orthonon Plate</i>								
Quartz.....	6.4	8.4	10.9	13.6	16.5	19.8	23.4	27.3
Soda-lead.....	5.2	7.3	9.8	12.5	15.5	18.7	22.3	26.0
Soda-lime.....	6.2	8.0	10.0	12.4	15.0	17.8	20.8	24.0
Boro-silicate.....	4.7	6.3	8.3	10.5	12.9	15.6	18.5	21.5
C-2 daylight.....	8.0	10.9	14.3	18.2	22.5	27.1	32.2	37.3
C-3 photographic....	13.7	18.9	24.6	31.2	38.6	46.6	55.2	64.3
<i>Panchromatic Plate</i>								
Quartz.....	2.3	3.1	4.1	5.2	6.4	7.7	9.1	10.6
Soda-lead.....	2.1	2.9	3.8	4.9	6.1	7.4	8.9	10.4
Soda-lime.....	2.2	3.0	4.0	5.1	6.3	7.6	8.9	10.4
Boro-silicate.....	2.1	2.7	3.4	4.3	5.2	6.2	7.4	8.6
C-2 daylight.....	3.4	4.2	5.2	6.5	7.8	9.4	11.1	12.8
C-3 Photographic....	5.4	6.6	8.0	9.7	11.4	13.7	16.3	18.8

*In computing sensitivities of C-2 daylight and C-3 photographic lamps the average commercial values of transmitted luminous flux of 65 per cent. and 35 per cent., respectively, have been employed.

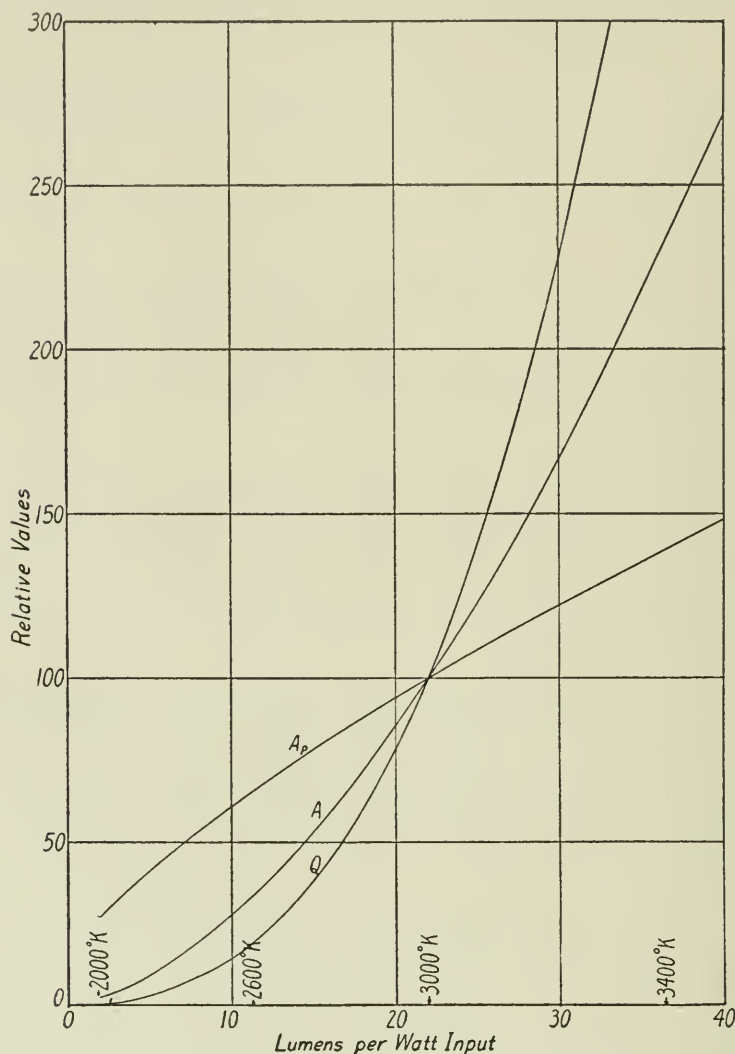
for the Seed's 26 plate only, since they are typical of all plates and glasses tested.

One of the authors has previously found that the transmission factors of colored glasses change with change in temperature. This would probably cause a minor error in our results, when these glasses are incorporated into lamp-bulbs, but the error need not

be taken into account for the glasses considered in this investigation. The error would be very large in the case of red glasses, for example.

The spectrograms of photographic lenses given in Fig. 6 show

FIG. 20.



Variation of actinicity (A), pseudo-actinicity (A_p), and photographic effectiveness (Q) with the luminous efficiency of the tungsten radiator in gas-filled bulb (Seed's 26 emulsion).

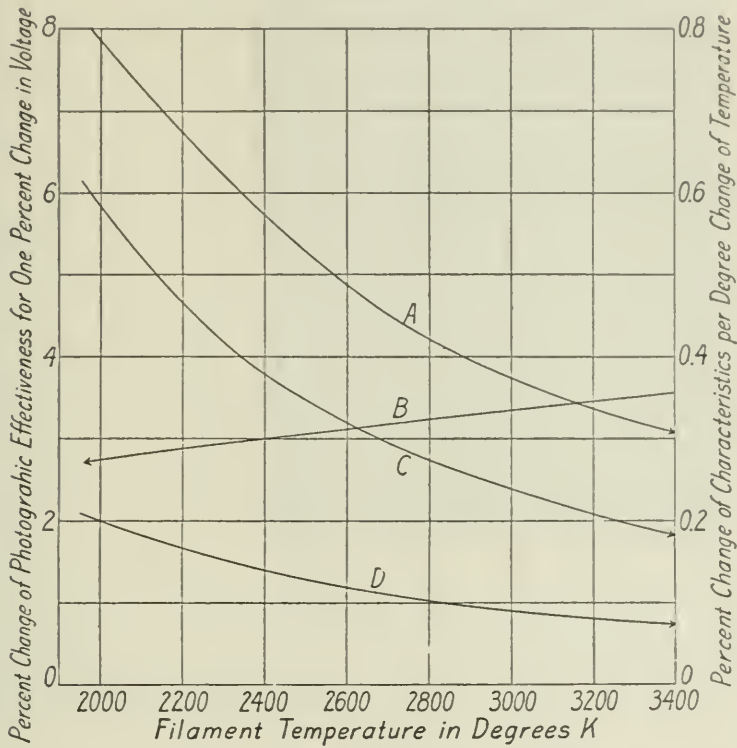
that commercial lenses cut off at a higher wave-length than do the lamp-bulb glasses.

VII. PSEUDO-ACTINICITY OF RADIATIONS FROM THE SUN AND GAS-FILLED TUNGSTEN FILAMENT LAMPS.

The arrangement of photographic apparatus was such that the radiation was first reflected from the plane first surface of a plate

glass, whence it traversed an oscillating three-ply non-selective wire-gauze screen, thence through another similar oscillating wire-gauze screen, thence finally through a ten-step rotating sector disc to the photographic plate. The plate glass was backed so as to absorb all radiation that traversed the plate and would normally be reflected at the back surface. The illumination was measured at the plate position with the second gauze screen

FIG. 21.

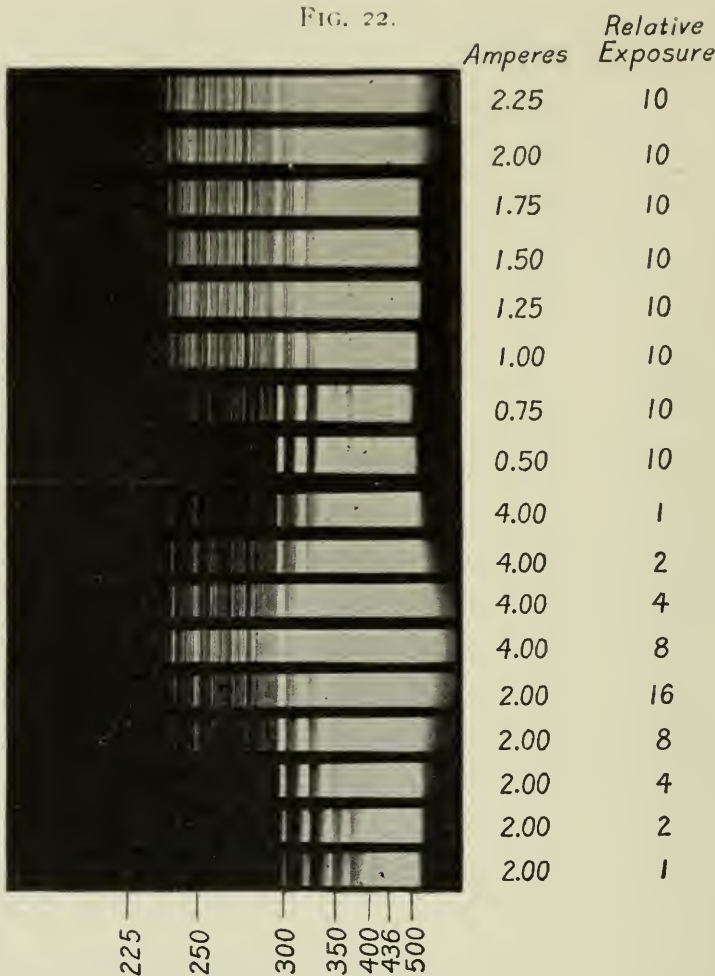


Percentage change in photographic effectiveness (A), actinicity (C), and pseudo-actinicity (D) for 1° C. change in filament temperature; percentage change in photographic effectiveness for 1 per cent. change in lamp voltage (B).

removed and the intensity of illumination upon the photographic plate was computed by multiplying the measured value by the transmission factor of the second gauze screen.

The photographic emulsions employed were 4" × 5" dry plates manufactured by the Eastman Kodak Company and were of the following types: Seed's 23, orthonon and Wratten M panchromatic.

The three sources of radiation were: a 1000-watt, 115-volt Mazda C lamp; a 1000-watt, 100-volt Mazda C-3 photographic lamp; and afternoon sun between 12.15 and 3 P.M., March, 1921. Results are given in Table XVI.



The ultra-violet spectra of the tungsten arc through quartz, at various currents and photographic exposures, as obtained by a quartz prism spectrograph.
(From "Ultra-violet Radiation" by M. Luckiesh.)

TABLE XI.

Table showing the actinicies of radiations from incandescent tungsten at various temperatures as measured by four types of photographic emulsions. These data were computed by multiplying the pseudo-actinicies in Table I by the values of lumens per watt given in Table VII, and dividing by 1000.

Type of plate.	Actinicity of radiations from tungsten at temperatures indicated.							
	2000° K.	2200°	2400°	2600°	2800°	3000°	3200°	3400°
Through quartz optical system alone.								
Seed's 26.....	0.0095	0.0305	0.071	0.146	0.265	0.442	0.695	1.035
Seed's 23.....	.0044	.0132	.030	.061	.108	.178	.279	0.410
Orthonon.....	.0117	.0345	.0775	.153	.266	.435	.675	.995
Panchromatic...	.0042	.0128	.029	.058	.103	.170	.262	.385
Through soda-lead glass.								
Seed's 26.....	0.0086	0.0270	0.064	0.132	0.234	0.390	0.605	0.900
Seed's 23.....	.0040	.0124	.0285	.0575	.101	.169	.262	.385
Orthonon.....	.0095	.0300	.070	.141	.250	.412	.640	.950
Panchromatic...	.0038	.0120	.027	.055	.098	.163	.256	.380

TABLE XII.

Table of relative values of the photographic effectiveness of radiations from incandescent tungsten at various temperatures through two kinds of media for four types of emulsions. These data are computed by multiplying the values of pseudo-actinicities given in Table I by the brightness of tungsten given in Table VII. To obtain absolute values multiply the tabulated values by $10^4 A \div 4d^2$ where d is the distance in cm. from the radiator of A sq. cm. area.

Types of plates.	Relative photographic effectiveness of radiant energy from incandescent tungsten at temperatures indicated.							
	2000° K.	2200	2400	2600	2800	3000	3200	3400° K.
<i>Through Quartz</i>								
Seed's 26.....	105.6	455	1610	4575	11,070	24,320	50,100	93,700
Seed's 23.....	48.7	197	676	1901	4,525	9,800	20,080	37,300
Orthonon.....	130.	517	1755	4786	11,140	23,950	48,450	90,100
Panchromatic.....	46.7	191	660	1830	4,322	9,320	18,840	34,960
<i>Through Soda-lead Glass</i>								
Seed's 26.....	95.4	406	1450	4120	9,790	21,420	43,700	81,500
Seed's 23.....	44.7	185	644	1795	4,254	9,320	18,840	34,960
Orthonon.....	105.6	449	1577	4400	10,470	22,630	46,160	85,800
Panchromatic.....	42.6	178	612	1725	4,120	8,950	18,420	34,330

TABLE XIII.

Table showing relative values of pseudo-actinicities A_p , actinicities A and photographic effectiveness Q , for the radiations from incandescent tungsten at indicated temperature (Kelvin) in terms of their values at a filament temperature of 3000° K.

	2000° K.	2200° K.	2400° K.	2600° K.	2800° K.	3000° K.	3200° K.	3400° K.
Relative values for Seed's 26 plates.								
A_p	26.5	37.3	50.8	66.1	81.9	100	119	139.5
A	2.2	6.9	16.4	33.9	60.0	100	155	231
Q	0.45	1.9	6.8	19.2	45.7	100	204	380
Relative values for orthonon plates.								
A_p	27.8	39.0	52.4	66.8	82.9	100	119	139
A	2.3	7.3	17.0	34.2	60.7	100	155	230
Q	0.47	2.0	7.0	19.6	46.3	100	204	380
Relative values for W. and W. panchromatic plates.								
A_p	28.4	39.2	51.4	66.2	82.4	100	120	140
A	2.3	7.3	16.5	33.7	60.5	100	157	233
Q	0.48	2.0	6.8	19.3	46.0	100	206	384

TABLE XIV.

Table showing rate of change of photographic characteristics of radiations from incandescent tungsten through soda-lead glass with definite changes in filament temperature (Kelvin) and voltage, these characteristics being measured by a Seed's 26 emulsion.

Rate of Change in Indicated Characteristics.

Filament temp. ° K.	For one degree change in filament temperature.			Resultant change in photographic effectiveness for 1 per cent. change in voltage.
	Photographic effectiveness.	Pseudo-actinicicy.	Actinicicy.	
2000	0.79%	0.20%	0.58%	2.75%
2200	.67	.165	.46	2.88
2400	.575	.14	.38	3.00
2600	.49	.12	.32	3.13
2800	.42	.10	.28	3.24
3000	.375	.09	.24	3.35
3200	.34	.08	.21	3.45
3400	.31	.075	.18	3.55

TABLE XV.

Table showing the photographic efficiencies of radiations from tungsten at various temperatures (Kelvin) after traversing various media, as measured by the sensitivities of the Seed's emulsions. These values, in per cent., are computed by multiplying the values of pseudo-actinicities in Table I by values of lumens per watt in Table VII, divided by ten times the sensitivities of the Seed's emulsions for radiations of wave-length 436 m μ given in Part V. Radiant energy of wave-length 436 m μ is taken as standard of 100 per cent. efficiency.

Interposed media.	Photographic efficiencies for tungsten radiation.							
	2000°	2200°	2400°	2600°	2800°	3000°	3200°	3400° K.
<i>Seed's 26 Emulsion</i>	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Quartz.....	.030	.095	.222	.458	.82	1.38	2.17	3.24
Soda-lead.....	.027	.085	.200	.413	.73	1.22	1.89	2.81
Soda-lime.....	.030	.092	.213	.430	.76	1.25	1.93	2.87
Boro-silicate.....	.025	.077	.180	.367	.65	1.08	1.68	2.50
C-2 daylight.....	.027	.085	.197	.405	.72	1.20	1.86	2.77
C-3 photographic....	.025	.078	.182	.374	.66	1.11	1.71	2.53
<i>Seed's 23 Emulsion</i>								
Quartz.....	.033	.098	.224	.458	.81	1.34	2.09	3.10
Soda-lead.....	.030	.092	.213	.432	.76	1.27	1.96	2.9
Soda-lime.....	.032	.095	.218	.441	.78	1.29	2.02	2.98
Boro-silicate.....	.029	.089	.202	.415	.74	1.22	1.92	2.85
C-2 daylight.....	.027	.086	.202	.415	.75	1.24	1.94	2.88
C-3 photographic....	.027	.086	.208	.424	.76	1.27	1.98	2.96

TABLE XVI.

Table of pseudo-actinicities of the radiant energy from afternoon sun, a Mazda C gas-filled tungsten lamp at approximately 2850°K., and a Mazda C-3 photographic lamp at approximately 3100°K., as measured by three types of photographic emulsions. Illumination measured at the plate position in all cases.

Type of radiator.	Type of plate.	Pseudo-actinicities.	
		Actual.	Relative.
1000-watt Mazda C.....	Seed's 23	6.69	.51
1000-watt C-3 photographic.....	Seed's 23	9.09	.69
Afternoon sun.....	Seed's 23	13.19	1.00
1000-watt Mazda C.....	Orthonon	9.13	.56
1000-watt C-3 photographic.....	Orthonon	14.82	.90
Afternoon sun.....	Orthonon	16.42	1.00
1000-watt Mazda C.....	Panchromatic	3.72	.50
1000-watt C-3 photographic.....	Panchromatic	4.96	.67
Afternoon sun.....	Panchromatic	7.42	1.00

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⁴ *Proc. Roy. Soc.*, 1917, 33.
⁵ A. J. PACINI: "Ultra-violet Therapy," 1923.
⁶ M. LUCKIESH: *Elec. World*, **64**, 1914, 129 and 954; *Trans. I.E.S.*, **10**, 1915, 149.
⁷ M. LUCKIESH: *JOUR. FRANK. INST.*, **186**, 1918, 111; "Color and Its Applications" (Van Nostrand), 2nd Ed., 1921, 399.
⁸ JONES, HODGSON and HUSE: *Trans. I.E.S.*, **10**, 1915, 963.
⁹ *Jour. Opt. Soc. Amer.*, **4**, Sept., 1920, 305.
¹⁰ *Bull. Bur. Stds.*, **13**, 1916, 459.
¹¹ *Phys. Rev.*, **10**, Oct., 1917, 377.
¹² *Astrophys. Jour.*, **45**, April, 1917, 149.
¹³ Bulletin No. 153, *Amer. Inst. Min. and Met. Engrs.*, Sept., 1919.
¹⁴ *Trans. I.E.S.*, **16**, 1921, 419; *JOUR. FRANK. INST.*, **192**, 1921, 109.
¹⁵ *Jour. Amer. Ceramic Soc.*, **2**, 1919, 743; *Trans. I.E.S.*, **17**, 1922, 600.
¹⁶ Since the completion of this manuscript there has come to the notice of the authors a paper proposing certain new photographic units by L. A. JONES, *Illum. Eng.* (London), **15**, Sept., 1922, p. 247. Communication No. 135 from the Research Laboratory of the Eastman Kodak Company.

THE editor of *The Bell System Technical Journal* comments thus on the subject of the first paper in the second number of this periodical "The electric wave-filter, an invention of Doctor Campbell,

is one of the most important of present-day circuit developments, being indispensable in many branches of electrical communication. It makes possible the separation of a broad band of frequencies into narrow bands in any desired manner. . . . As the communication art develops, the need will arise to transmit a growing number of telephone and telegraph messages on a given pair of wires and a growing number of radio messages through the ether, and the filter will prove increasingly useful in coping with this situation. The filter stands beside the vacuum tube as one of the two devices making carrier telephony and telegraphy practicable, being used in standard carrier equipment to separate the various carrier frequencies. It is a part of every telephone repeater set cutting out and preventing the amplification of extreme line frequencies for which the line is not accurately balanced by its balancing network. It is being applied to certain types of composite lines for the separation of the d.c. Morse channels from the telephone channel. It is finding many applications to radio of which multiplex radio is an illustration." G. F. S.

The Lowest Temperature Yet Obtained.—In a communication in the *Transactions of the Faraday Society* (1922, 18, 145). Dr. Kamerlingh Onnes gives in detail some results recently obtained by him, in which the temperature of liquid helium has been brought to within less than a degree of the absolute zero. The liquefaction of helium having been successfully accomplished, efforts were made to freeze it. The method adopted is that of evaporation under reduced pressure. The initial procedure is with liquid hydrogen. A large volume of this was made, incidental to which operation the preparation of about twice the volume of liquid air was necessary. The helium was converted into a liquid and then allowed to evaporate under favorable conditions, the course of the evaporation being closely watched with care not to cause any elevation of temperature in the liquid. No evidence of solidification was obtained, the liquid preserving its mobility throughout the procedure. Onnes expresses the view that in the experiment he had reached a temperature within less than one degree of the absolute zero, the point being taken as 0.82° K. As a conservative estimate he prefers to give the temperature at some hundredths of a degree below 0.9° K. Onnes considers it possible that helium may not solidify at the absolute zero. However, he calls attention to the fact that other problems in science have been regarded as unsolvable, and yet have been fully solved. Even in this field, the study of which was begun by Faraday, who showed the possibility of liquefying many of the common gases, there was at first a disposition to place certain gases in the "permanent" list, regarding them as incapable of liquefaction, but all these have yielded to patient investigation. H. L.

THE COLORING OF THE DIAMOND BY RADIUM RADIATION.*

BY

S. C. LIND, Ph.D., and D. C. BARDWELL.

THE results of various investigators attempting to color the diamond by radium radiation have not been entirely uniform and in the main were unsuccessful. Doelter¹ classes diamond as the most difficult of all minerals to color, and reports for the most part failures or very slight coloring. On the other hand, Crookes² obtained in a few cases bluish-green and sage-green colors and A. Miethe³ produced a yellow color from a colorless diamond in one instance.

As reported in the preceding paper,⁴ all minerals except diamond, that can be colored by radium radiation, are colored by the penetrating (beta and gamma) rays transmitted through the glass tube containing the radium salt. Experiments of this character, using 250 mgs. Ra for thirty days on five Cape diamonds of four to ten carats of bright straw-yellow color, failed in all cases to produce any change in color. Two other cut diamonds of the same color were sealed inside a tube with 10 per cent. RaCl_2 for the same length of time. The one which was entirely covered by the 10 per cent. salt became fairly green (about a half grass-green) in thirty days, while the other, lying on the surface of the salt, took on a distinct but fainter green.

It was therefore quite evident that direct (probably alpha) radiation is necessary to color the diamond. This experiment explains why most investigators, working with penetrating radiation only, have failed to produce color changes.⁵ To confirm this,

* Communicated by Dr. R. B. Moore, Chief Chemist, U. S. Bureau of Mines and Associate Editor of this JOURNAL. Communication from the Rare and Precious Metals Experiment Station, U. S. Bureau of Mines, in Coöperation with the University of Nevada. Published by permission of the Director, U. S. Bureau of Mines.

¹ C. Doelter, "Das Radium und die Farben," Steinkopff, Dresden, 1910, p. 123.

² Sir Wm. Crookes, *Proc. Roy. Soc.*, **74**, 47 (1904); *Nature*, **94**, 300 (1914); *Phil. Tr. Roy. Soc.*, **214A**, 433-45 (1914); *Sci. Amer. Supplement*, No. 2270 (July 5, 1919).

³ A. Miethe, *Ann. d. Phys.*, **19**, 633 (1906).

⁴ *Jour. Frank. Inst.*, September, 1923, p. 375.

⁵ Crookes (*loc. cit.*), who obtained positive results, worked with the direct radiation of radium salts.

four straw-yellow Cape cut diamonds of two to six carats were completely covered with 10 per cent. RaCl_2 , sealed in a glass tube, and left for seventy-five days. A deep grass or sage-green was produced which was of quite uniform shade in all and, as far as could be detected, seemed to penetrate through the crystal. No trace of the yellow color appeared to remain.

The apparently deep penetration of color is very surprising, since alpha rays can penetrate diamond to a depth of the order of 0.001 inch only. This will be more fully discussed later. The non-penetrating character of alpha radiation also led to a second consideration, namely, that alpha rays will be able to reach the surface of the diamond only from those layers of salt immediately in contact with it (from a layer less than 0.001 inch). The rest of the salt absorbs its own alpha radiation and is wholly ineffective in producing any color changes. This suggested that radium emanation could be much more effectively employed, since at low gas pressure, the absorption in a container not too large will be practically negligible, and the proportion of effective radiation will depend principally upon the ratio:
$$\frac{\text{area of diamonds exposed}}{\text{total area exposed}}.$$

Accordingly seven cut diamonds from 1.5 to 9.5 carats, of original color white to yellow, were sealed in a glass tube (about 10 cms. long and 1.5 cms. in diameter) with 114 millicuries (m.c.) initial radium emanation. The fluorescence was marked in all cases but not uniform, varying through greenish-blue to bluish-green shades without reference to the original color of the stones, which were supposed to represent one Brazilian and all the principal South African fields.⁶ That the intensity of radiation was greater than in 10 per cent. salt was evident from the increased rate of coloring, though this cannot be accurately judged owing to the rapid coloring of the glass tube container. After an exposure of nine days, during which time 91.4 m.c. of emanation disintegrated, the tube was opened and all seven were found to be colored a moderate shade of green. They were put into another tube of the same dimensions and exposed for nine days to an initial quantity of 161 m.c. of emanation. At the end of this time all had deepened in green shade and were nearly as deep as the ones exposed for seventy-five days to 10 per cent. RaCl_2 . A third exposure was

⁶ Since all the diamonds examined had passed through commercial channels their origin cannot be given with certainty.

begun, but was continued for only a few hours, owing to the cracking of the glass tube. Upon examining some of the diamonds visually it was observed that they had apparently developed "carbon spots."⁷ This was very puzzling, as "carbon spots" have never been reported as being produced artificially. The original crystals had been perfect, nor had any "carbon spots" been produced in the four diamonds colored to a deeper shade of green by 10 per cent. RaCl_2 . Attempts to remove the spots chemically by washing in ammonia, hot HNO_3 , hot chromic mixture, organic solvents, etc., failed. Examination under the high-power microscope revealed round black spots like fly specks at a considerable depth below the surface (as much as 1 to 2 mm.), a few of which were surrounded by lighter brown halos as if the "carbonization" process were spreading from a centre.

The rest of the investigation was devoted to an attempt to solve the puzzling problems presented by the coloring and the "carbon spots," in connection with the nature of the latter, and the production of both at depth beyond the range of alpha particles in the diamond.

The coloring itself can be described in a few words. In five specimens of light-yellow cut diamonds no color by penetrating rays (through glass $\frac{1}{2}$ to 1 mm. thick) could be produced in thirty days, as already stated. In more than thirty specimens of cut and one uncut diamond varying in color from colorless to yellow to brown, no failure to produce color by direct contact with radium salt or radium emanation was encountered. Green and only green color was produced; even the shade was the same for the same radiation intensity and the same original color. Prolonged heating to 500°C . restores the *original* color, leaving one to suppose that the green color is superimposed and merely masks the original color.

An estimation of the initial alpha radiation from emanation received per unit surface of diamond, in the experiment where "carbon spots" were first obtained, indicated that the alpha ray intensity was about five-fold that in the case of diamonds buried in 10 per cent. RaCl_2 , when no spots were developed. Assuming that intensity is the controlling factor, exposure in 50 per cent. RaCl_2 ought to produce "carbon spots" also. A test was made

⁷ Small specks of carbon, possibly graphite, which frequently are found in natural diamonds.

with four Cape cut diamonds of about two carats each (three white and one slightly yellow) buried in 50 per cent. RaCl_2 for seventy-four days. A very deep grass or emerald green color was produced, practically identical in shade in all cases, but no "carbon spots" were produced. In all later experiments it was found that "carbon spots" are produced only in contact with emanation, never in salt, but not universally even in emanation, nor could we determine the factor which controls the carbonization. It was apparently not a characteristic inherent in the individual diamonds, because there were no variations among different specimens under the same conditions; either all or none developed "carbon spots" in a given test. One light yellow cut diamond of eight carats, which developed "carbon spots" in emanation and from which they had been removed (see later), failed to develop any on being radiated with 50 per cent. RaCl_2 till it again colored green.

The nature of the spots also remained unsolved. It appeared plausible to suppose that under radiation, diamond, which is known to be an unstable form of carbon at ordinary temperature and pressure, should revert to the stable form graphite, just as white phosphorous has been shown to be converted to red by radium radiation.⁸ That such a process might be taking place appeared probable from the brown halos surrounding a few of the spots. To explain the localization of discrete spots, rather than a general darkening similar to that observed by Crookes⁹ under cathode-ray bombardment, it appeared plausible to suppose that there exist initial "seeding centres" where the change originates and from which it spreads. This theory was greatly shaken if not entirely upset by the observation that prolonged heating in air at a red glow caused the "carbon spots" to disappear permanently. We can hardly assume a reversion to diamond under these experimental conditions. We cannot attribute it to oxidation unless we assume the diffusion of oxygen into and possibly the diffusion of CO_2 or CO out of the diamond. A very ingenious hypothesis was proposed by Dr. R. B. Moore, namely, that there may be in the diamond minute pockets of CO_2 or CO under high pressure, not detectable by the microscope, which may be decomposed by the radiation into C and O_2 which recombine *in loco* upon heating. CO is the more probable, since CO_2 is very slightly

⁸ H. Becquerel, *Comp. Rend.*, **133**, 709-12 (1901).

⁹ Sir Wm. Crookes, *Sci. Amer. Supplement*, No. 2270 (1919).

decomposed, even by intense alpha radiation.¹⁰ The depth of the pockets from the surface also imposes a difficulty since they cannot be reached by alpha rays, and beta and gamma rays are much less effective in producing chemical action. This theory also does not conform with the idea of gradual growth (brown halos); some of the spots become large enough to be visible to the naked eye, and all of them are easily visible with a small hand lens. That the spots are in reality some form of carbon is supported by the fact that the simultaneous exposure in emanation of a large number of different transparent minerals, together with the diamond, gave these spots only in the latter.

A most puzzling question is the explanation of any effect, either production of color or of "carbon spots," at a depth in the crystal exceeding the range of alpha rays—if one is to suppose the effect due to alpha rays. The question may be divided into two: (1) Are we sure that the effects are deeper than the alpha ray range? (2) Are they due to alpha rays? (1) There can be no doubt about the depth of the carbon spots below the surface, which were observed by the microscope (change of focus) and confirmed by the diamond-cutter who stated it would be necessary to cut away one-half to two-thirds of the crystals (of several carats) to remove the spots. In regard to the depth of penetration of *color* there is much doubt, and that point will therefore be referred to again. Question (2) can best be considered generally for either effect as follows:

The possibilities of the production of effects beyond the range of alpha rays appear to be the following: (a) By penetrating (beta or gamma) rays; (b) by soft beta rays which could not penetrate the wall of the glass container, but which do penetrate diamond sufficiently to produce the effects observed; (c) by a secondary penetrating radiation set up at the diamond surface by some form of non-penetrating radiation (including alpha rays); (d) by transmission by an electronic or atomic "chain effect" of a disturbance set up at the surface, possibly equivalent to (c); (e) (applying to color only) by the diffusion through the crystal of color produced at the surface. Hypothesis (a) can apparently be dismissed by comparing the negative results of exposure outside a tube with the positive ones inside. The possibility of (b) is not excluded, but it should be remembered that such soft radia-

¹⁰ E. E. Wourtsel, *Le Radium*, **11**, 346 (1919).

tion could not extend the depth beyond a layer equivalent to $\frac{1}{2}$ to 1 mm. of glass, which would be insufficient to penetrate the entire crystal in the case of large diamonds. Regarding (*c*), no such form of radiation in diamond is known, nor would the low atomic weight of carbon indicate that it would have much penetration; on the other hand, not much would be required, for the same reason. Both (*d*) and (*e*) appear intangible at present. None of these hypotheses receives any support from the observations of Joly¹¹ and of Rutherford¹² on pleochroic halos in mica, which have been shown to have exactly the diameter predicted by the range of alpha rays emitted from a point source, and which have persisted through geological periods of time.

We are therefore forced to leave the question of the penetration of the effects unsettled in regard to "carbon spots" and will conclude the discussion with the observations contained in the following paragraphs on the penetration of color.

As far as can be determined optically (even by gem experts), either with the unaided eye or with the microscope, the color produced in diamonds persists throughout the crystal. On the other hand, this is not consistent with a direct alpha-ray effect, though rigidly it does not need to be, since "carbon spots" are produced by some influence beyond the alpha-ray range and possibly color also. But color production is a much more general phenomenon than that of carbonization and need not be produced by the same radiation. Crookes (*loc. cit.*) found that the removal of the surface from a cut diamond destroys the color. This would appear to show that it is a surface coloring only, but it must be remembered that cutting or grinding a substance of such hardness is a prolonged process involving the generation of much heat, so that the destruction of color may be due to a heat effect.¹³

Two attempts were made to solve the question without cutting or grinding. A small brown cut diamond was colored green by

¹¹ J. Joly, "Radioactivity and Geology" (1909), pp. 64-9; *Phil. Mag.* (6), 19, 327 (1910).

¹² E. E. Rutherford, "Radioactive Substances and Their Radiation" (1913), p. 310.

¹³ It is interesting in this connection that in 1915, F. P. Mennell (*Mineralogical Magazine*, 17, 202) described the occurrence of natural green diamonds in an alluvial field situated on the borders of the Somabula Forest in Southern Rhodesia. He states that the color is entirely lost in the usual course of cutting and polishing for use in jewelry.

radiation and then broken into two or three fragments. Examination under a high-power microscope failed to reveal any surface zone of color; each fragment with a colored (polished) surface appeared to be colored throughout, but the reflection and diffraction of green light from the polished (green colored) surfaces was so great that one could not be sure that the appearance of internal color was not merely due to an optical effect. The masking of an internal yellow or brown by green seems to demand more than a thin surface layer of green, but again one must recall that this thin green layer is at polished surfaces from which light is reflected in all directions, and also that the masking is *not* complete in *thick brown* crystals. An uncut chip of colorless diamond was colored green by radiation and then cleaved into two pieces. Viewed through the cleavage plane, the fragment still looked green, but again one could not be sure it was not due to reflection. The question might be settled by covering all the facets but one with foil or paint during radiation, and later covering the colored surface with an opaque covering and looking through the others. This experiment was not attempted.

The question of the color penetration remains unsettled with some evidence in favor of non-penetration, which, however, is not conclusive.

The question of the permanency of the green color to light is a much simpler one. Experiments, both in diffused and direct sunlight, showed that the color is quite permanent, perhaps in the same class with glass colored by radiation, though the observations have not yet extended over so long a period as with glass. This confirms the general rule already stated, that the more difficult a mineral is to color the more permanent the color. As stated, the color can be removed by heating to 500° or higher for half an hour or less (depending on the temperature). In this way green color can be toned down in shade by interrupting the heating at the desired point.

The question of imparting permanent radioactivity to the diamond by radiation by radium, which was the subject of experiments by Sir Wm. Crookes (*loc. cit.*), has not been investigated in the present work, but there seems to be no reason to believe this cannot be explained by "active deposit" (or radium itself in case of contact with radium salt), in the light of adsorption and surface phenomena as now explained by Langmuir and others.

SUMMARY.

1. Diamond is not colored by the penetrating (beta and gamma) radiation from radium salt in glass tubes 0.5 to 1 mm. thick.

2. Diamond is always colored green by direct radiation, either from high-grade radium salts or from the gas, radium emanation. No exceptions were met in more than thirty specimens.

3. The green color is apparently light-permanent, but can be removed by heating to a dull red.

4. Yellow and brown diamonds are also colored green, but are restored by heating to their original colors. In the case of large deep brown stones the color masking by green was not complete.

5. Recutting the crystal after coloring removes the green color. This is possibly a heat effect during cutting, and does not prove that the coloring is merely a surface effect.

6. The depth of penetration of the color zone could not be determined. If it is an alpha-ray effect, it would be limited by the range of alpha rays in diamond, about 0.001 inch. But reflection of green light from the highly polished surface interferes with optical observations.

7. Radiation by emanation is more effective than by salts, owing to the greater absorption of alpha rays by the salt itself.

8. In some cases in emanation, but never in salt, the radiation resulted in the production of "carbon spots" in the interior of the crystal. The black spots are probably a form of carbon, the nature of which was not definitely determined. They can be removed by prolonged heating in a blast flame.

9. The "carbon spots" are undoubtedly beyond the range of alpha rays in the crystals, which suggests that the color may be penetrating also and that both are produced by some form of secondary radiation more penetrating than alpha rays.

Waxy Coating of the Apple. CHARLES E. SANDO, of the Bureau of Plant Industry, U. S. Department of Agriculture (*Jour. Biol. Chem.*, 1923, **56**, 457-468), has studied the constituents of the wax-like coating on the surface of the apple, using Ben Davis varieties. Several hydrocarbons and alcohols were isolated; the chief constituents were triacontane, $C_{30}H_{62}$; a paraffin hydrocarbon, heptacosanol; $C_{27}H_{56}O$, a secondary alcohol, and malol, $C_{30}H_{48}O_3$, a new crystalline dextrorotatory alcohol which contains at least two hydroxyl groups.

J. S. H.

AN ANALYSIS OF THE AUTOMOBILE HEADLIGHT PROBLEM.*

BY

P. G. NUTTING, Ph.D.

Consulting Optical Engineer.

FIFTEEN years of active investigation, invention and experimenting have failed to produce safe and efficient means of headlighting automobiles. Scores of different types of headlighting appliances have been produced and are in use, yet the best of these are but little better than the best of fifteen years ago, while the worst is fully as bad as the poorest of that date. Most states have enacted legislation intended to correct headlighting evils but, with one or two exceptions, these have been by no means effective. Meanwhile accidents due to defective headlighting are steadily increasing.

The optical engineers of this country must accept the major share of the responsibility for such a state of affairs. They alone can state when the best possible solution of this difficult problem has been attained. They alone can set limits of tolerance, devise adequate tests and outline specifications and remedial legislation. The driving public is a fairly good judge of efficient headlighting, and the consensus of public opinion is undoubtedly that the problem of headlighting has *not* been solved. The impression is widespread that it cannot be completely solved.

The practical requirements—essential, desirable, and agreeable—of road lighting for safety, convenience, and pleasure have been discussed in dozens of papers and in many reports of committees of the Illuminating Engineering Society and the Society of Automotive Engineers and are familiar to every experienced driver. Means of meeting these requirements have yet received but scant mention, apparently because of a wish to avoid an appearance of commercial bias. The interests of the public, however, demand an impartial, competent analysis of the optical engineering aspects of the problem of headlighting, coupled with

* Communicated by the Author.

specific recommendations as to best practice, tolerances, inspection and safety rules, all from the independent viewpoint of the public itself, regardless of commercial consequences.

AUTOMOBILE HEADLIGHTING REQUIREMENTS.

The safe driving of automobiles at night requires: (1) Beam lighting at a distance ahead on the road, (2) uniform lighting of the driving headway, (3) absence of intense lighting (glare) to the left and above the road in the middle distance.

(1) The beam lighting must be sufficiently intense to clearly illuminate a straight level road 100 to 200 feet ahead, and to clearly pick up pedestrians and unlighted vehicles of a dark shade at a distance of 150 feet. This means a beam candle-power of 5000 to 15,000. Only moderate road curvatures are to be cared for by beam lighting since sharp turns are taken at reduced speed and are lighted at a wide angle by the foreground light.

(2) The foreground lighting must have sufficient spread and intensity for safely negotiating street corners and at the same time light the road straight ahead in the middle distance sufficiently for safe driving. This means an illumination of about a foot candle on the road ahead of the machine with a spread of 15 or 20 feet, shading off laterally in intensity. To produce such lighting there is required some special device intermediate between the parabolic reflector (beam lighting) and the completely diffusing screen as source.

(3) Unsafe glare is avoided by the elimination of high intensities 60 inches above the road and the same distance to the left of the left-hand headlight for a distance of at least 50 feet ahead. This limit of tolerance is usually set at 800 candle-power, about a tenth that within the direct beam. This limit is liberal in view of the optical difficulties of providing a beam with so sharp an intensity gradient at one edge. Good drivers meeting good drivers prefer plenty of light, keep their eyes on the road and away from headlights. Timid and inexperienced drivers passing reckless drivers having illegal or improperly adjusted headlights meet with the greater portion of headlight accidents.

The best headlighting then is that which provides a nearly uniform illumination of about one foot candle (in the driver's line of vision) on the road at all distances from the near foreground to at least 100 feet ahead directly in front of the car and

shading off gradually to right and left and sharply above the horizontal.¹ From two to five times that illumination is probably preferable if glare be carefully eliminated. Less than one-tenth that illumination in either the foreground, middle distance or extreme distance is unsafe in general. On lighted streets, foreground lighting is of chief consequence, on country highways, distant beam lighting.

In practice such ideal headlighting is almost unknown, since very few headlamps are capable of giving it even when carefully adjusted. Instead all sorts of headlighting evils are encountered, most of them far worse than that produced by a simple mirror with plane front glass if properly focused and directed. Undoubtedly the worst evil is the spread beam directed upward by faulty adjustment or bent supports. There is no escape from its dazzling glare while the headway is almost unlighted. A very common defect, occurring with many forms of patented front glasses, is too great concentration of light in the middle distance, frequently combined with too great lateral spread. This means insufficient distant light for safe rapid driving, and, if too widely spread, considerable glare at the critical period of approach. In the headlamps of many small cars no provision at all is made for distant lighting. Other less common headlighting defects are confusing checkerboard light patterns on the road caused by improperly designed prismatic front glasses, and front glass dazzle caused by lens-shaped (spherical or cylindrical) projections on the front glass. Such lens-shaped surfaces, or even rounded corners on prismatic surfaces, of course, should never be tolerated without a visor, for each forms a secondary image of the light source nearly as bright as the source itself, and each image throws light laterally over a wide angle.

PRACTICAL HEADLIGHTING.

Prerequisite in all safe and efficient headlighting are of course a good mirror and a highly concentrated lamp filament, otherwise there can be no control over the direction the light shall take. Fortunately both are available. Metal mirrors spun of soft metal and silver plated are available in a variety of sizes sufficiently perfect in form for all headlighting purposes. Within the past

¹ See report of the Committee on Motor Vehicle Lighting, *Trans. Ill. Eng. Soc.*, Feb., 1922.

two years the headlight lamp problem has also been solved. Lamps are now available having filaments less than $2 \times 2 \times 0.5$ mm., well centred in tipless bulbs. A 2-mm. filament at the focus of a mirror of 1-inch focal length provides an image spread of 12 feet at a distance of 150 feet. This is sufficiently small to permit good beam control and allows some leeway for slight imperfections of mirror and front glass. Lamps with large filaments or bulbs with tips are not to be tolerated. Means of adjusting the lamp in all directions by the driver have not found favor chiefly because their use requires the driver's attention on short turns and changes in grade just when he is most occupied with driving.

In order to secure sufficient distant lighting, roughly 10,000 (5000 to 15,000) beam candle-power must be provided. A lamp with 2-mm. filament in a mirror of 1-inch focal length sends out a beam with a spread of about .0065 steradian. The mirror subtends about 10 steradians, hence a 21 candle-power lamp of proper design can provide about 30,000 beam candle-power—fully double that required. This conclusion may readily be confirmed by a practical test. On the other hand, such a headlamp provided with a highly diffusing front could not give a foot candle of illumination at more than 10 feet away. Obviously beam lighting must be retained in part, the surplus light (about half the whole) being pulled downward to light the middle distance from 10 to 60 feet ahead of the car. The beam proper, with normal spread on a level road, provides the lighting from 50 feet ahead to the horizon. In practice losses by absorption and scatter at the lamp bulb, mirror surface and front glass average perhaps 50 per cent. of the beam.

Foreground lighting may readily be provided in several ways. The immediate foreground is amply lighted (to one foot candle) by light directly from the lamp if not unduly scattered by the front glass. The use of a weakly diffusing (frosted, ribbed or dimpled) front glass gives more light in the middle distance since such glass transmits the bulk of the incident light with but a small deviation. Such glasses can, however, be used only with a visor to obviate glare and waste of light above the horizontal. Front glasses partly covered with small pressed prisms of appropriate angle, base downward, pull part of the beam downward upon the road in the middle distance. The angular deviation

produced by such prisms is roughly half the prism angle, so that the appropriate angles range from 7° to 30° . An angle of 30° is about the greatest feasible in good pressed glass, hence 14 feet ahead of the car is about as near as it is feasible to refract light by means of prisms.

Replacing the ordinary parabolic mirror of the headlamp by an ellipsoidal mirror of proper ellipticity is an efficient and flexible means of securing the proper distribution of light on the road. If the ellipticity is high, the lighting approaches beam lighting with parabolic mirror; if low, the lighting approaches direct lighting from a lamp or highly diffusing source. An ellipsoid having a major diameter about twice the minor diameters gives a good distribution. The lower front quarter is cut away or left unsilvered for the escape of light while the visor effect of the upper front quarter (obviating all glare) is retained.

In principle there are two, and but two, means of avoiding glare: (1) Using an accurately *focused beam* from a clean parabolic mirror and small lamp filament and (2) using the headlamp at the rear end of an opaque *tubular shield*. The first is an ideal to be approached only with high-grade equipment in nearly perfect adjustment. Foreground lighting is provided by a partially prismatic front glass or by using an ellipsoidal departure from the parabolic mirror. The tubular shield (2) may be made as effective against glare as desired, but in practice is made of minimum length, so as not to be ungainly, and the bottom is left open to light the road in the foreground. It thus becomes in effect an enlarged visor of special design. With proper trim and bottom opening, a wide variety of front glasses, giving almost any desired light distribution on the road, is quite feasible.

The three requirements for safe and efficient headlighting may therefore be met by three different types of headlighting appliances as follows:

(A) Both headlamps consisting of specially designed ellipsoidal mirrors, each provided with a tipless lamp having a filament not over $2 \times 2 \times 0.5$ mm.

(B) Both headlamps consisting of the usual parabolic mirror and housing but provided with special front glasses, each approximately one-half plane and the other half refracting or weakly diffusing or both. If the diffusing type be used, it must be provided with an opaque visor to obviate glare.

(C) One headlamp (preferably that on the right) provided with clear glass front and focused for distant beam lighting, while the left-hand headlamp is provided with a prismatic or diffusing front glass and an opaque visor.

Existing headlamps most nearly satisfying all these requirements are chiefly of class *B*. Those of class *A* would be supplied with the car while those of classes *B* and *C* involve but minor, inexpensive parts of the ordinary headlamp assembly readily obtainable. Headlamps of class *A* are appropriate to high-priced, class *B* to medium-priced cars, while those of class *C* are best adapted for use on the lowest priced cars, being quite as efficient but not as attractive in appearance as those of classes *A* and *B*.

ACCIDENT PREVENTION.

The ultimate problem of eliminating accidents due to defective lighting involves much more than a solution of the headlighting problem, namely, the complete elimination of defective lighting. First, the driving public must be educated to know and demand good headlighting equipment kept in adjustment. Again, those driving cars must be taught to avoid directly viewing approaching headlights. An experienced driver, keeping his eyes on his own headway is in little danger from any headlights, however glaring.

Of by far the greatest importance is the setting of definite specifications and tolerances in headlighting performance and providing means for their rigid enforcement by test, adjustment or replacement and penalty for non-compliance. In a few states headlighting laws provide for testing and adjusting stations as well as outlining specifications and tolerances. This is of course the logical procedure since it is the headlighting *performance* not the *equipment* which is correct or at fault. The same equipment may give either very good or very poor headlighting, depending upon its adjustment.

SUMMARY.

The headlighting requirements for safe driving are:

(1) Beam lighting for picking up distant unlighted objects of not less than 5000 nor over 15,000 beam candles, centred on the road between 100 and 150 feet ahead with a maximum spread of not less than 10 nor over 30 feet.

(2) Foreground lighting for the driving headway, short turns and turnouts of not less than 0.1 nor over 5 foot candles from 3 to 60 feet directly ahead, with a spread of at least 20 feet.

(3) Limited lighting in the direction of the eyes of an approaching driver, not over 500 beam candle-power in a direction 60 inches above the road level, 60 inches to the left of the nearest headlight and 60 feet ahead.

Requirements 1 and 3 are met by the combination of the ordinary parabolic mirror, plane glass front and 21 cp lamp with filament not over $2 \times 2 \times 0.5$ mm., well focused. Requirements 2 and 3 are met by the ordinary lamp and mirror provided with either prismatic glass front or diffusing (ground, ribbed or dimpled) glass front with opaque visor or by a combination of all three. Requirements 1, 2 and 3 are all met by any one of three different types of equipment:

(a) A pair of headlamps each comprising an ellipsoidal mirror of suitable ellipticity and a lamp having a filament not over $2 \times 2 \times 0.5$ mm., properly focused.

(b) A pair of headlamps each comprising an ordinary parabolic mirror, lamp having a filament not over $2 \times 2 \times 0.5$ mm. in the focus of that mirror and a front glass one-third to one-half plane and the remainder either prismatic or weakly diffusing or both, the diffusing portion being covered with a visor of suitable design.

(c) One headlamp comprising a parabolic mirror, lamp and plane front glass adjusted for distant beam lighting, the other comprising mirror, lamp, prismatic or diffusing front glass and visor for lighting the foreground and middle distance.

The elimination of accidents due to defective headlighting involves:

Providing proper headlighting equipment and adjustment.

Educating the driving public to appreciate and demand good headlighting and to avoid looking directly at headlights while passing.

Enacting enforceable laws not only setting limits of tolerance in headlighting, but providing for testing and adjusting stations and penalties.

Eliminating the reckless driver.

A Wide Angle Lens for Cloud Recording. W. N. BOND. (*Phil. Mag.*, Nov., 1922.)—A whole hemisphere should be included in the field of view of a lens used to photograph all the clouds in the sky or to record flashes of lightning. A hemispherical lens with its plane surface horizontal and uppermost approximately meets this requirement and forms a sufficiently sharp image on a horizontal plate placed beneath the lens. The lens must be covered by a thin opaque screen having a small circular hole over the centre of the lens. This insures that all rays traversing the lens shall meet the hemispherical surface at right angles. A further improvement is made by covering this screen by a plane plate of glass, which avoids the exclusion from the circular aperture of rays at grazing incidence by the screen, thin though it may be. A monochromatic filter takes care of the chromatic aberration of the lens.

The image formed is circular. Objects at the zenith appear at the centre, while around the circumference are ranged the objects at the horizon. "It may be mentioned that the lens gives views similar to those seen by a fish in water." G. F. S.

Changes in the Charge of an Alpha-particle Passing through Matter. G. H. HENDERSON. (*Proc. Roy. Soc.*, A 717.)—"It is remarkable that investigations on the velocity of alpha-particles have hitherto failed to detect with certainty particles with velocity less than about 8×10^8 cm. per second ($0.4 V_0$ where V_0 is the initial velocity of alpha-particles from RaCO). Thus the minimum observed energy was that which would be acquired by the alpha-particle falling through about 600,000 volts. It is surprising that particles with such enormous energy should vanish, leaving no trace." The velocity of a beam of the particles was reduced by passage through absorbing material. They were then deflected by a magnetic field and their effect on Schumann photographic plates was registered. They were found to darken the plate when their velocity had fallen to one-fourth of its initial value. An interesting and unexpected product of the experiment was the appearance of a band between the undeflected beam and the beam normally deflected by the field. This is explained as due to alpha-particles with but a single positive charge. The doubly charged particles will turn into helium at some time. The photograph showed in addition the effect of particles with no charge at all.

G. F. S.

Fluosilicic Acid.—The fluosilicic acid, H_2SiF_6 , of commerce usually contains from 10 to 25 per cent. of the absolute acid, and a product containing more than 30 per cent. of absolute acid has rarely been prepared. C. A. JACOBSON, of Johns Hopkins University (*Jour. Phys. Chem.*, 1923, 27, 577-580), has devised a method of vacuum distillation by means of which he has prepared a product containing 60.92 per cent. of absolute fluosilicic acid at room temperature 20° to 22° C.

J. S. H.

THE ABSOLUTE MOBILITIES OF NEGATIVE IONS IN AIR.*

BY

LEONARD B. LOEB, Ph.D.

National Research Fellowship, University of Chicago.

ALTHOUGH it appears as if the Rutherford¹ alternating current method of measuring the mobilities of negative ions were capable of yielding the greatest accuracy of any of the methods used, the values of the mobilities thus far obtained from it show variations which are far greater than are to be expected from the errors entering into the measurement. Thus in some very careful measurements made in 1910, Kovarick² found a mobility of the negative ions of 2.06 cm./sec. volt/cm., while the value obtained by Franck and Pohl,³ and since then by other workers, generally lay close to 1.8 cm./sec. In the experiments of Kovarick the ions were generated by ultra-violet light acting directly on one of the plates of the field in which the mobilities were measured (Fig. 4a). In order to measure the mobilities of the positive as well as of the negative ions Franck generated his ions in an auxiliary chamber *G* (Fig. 4b) by means of polonium. The ions were separated by means of a weak field *G* (termed the auxiliary field) between the plate *p* and the gauze *g* and driven through the meshes of the gauze into the alternating field *E* between *g* and the plate *e*. More recently the writer found that the mobilities of the negative ions measured directly on photoelectrically generated (from plate *p*, Fig. 4a) ions was 2.18 cm./sec., while the mobilities of the negative ions generated by polonium in an auxiliary chamber lay close to 1.84 cm./sec., the conditions otherwise being the same.

Investigation showed that the difference in mobility lay in the use of the gauze and auxiliary field and not in the nature of the ionizing agent, for ions generated photoelectrically from the plate *p* below the gauze *g* in Fig. 4b yielded a mobility of 1.87 cm./sec. under nearly the same conditions that gave a mobility of 1.84 cm./sec. with the polonium ions. These experiments indicated

* Communicated by Dr. W. F. G. Swann, Associate Editor of this JOURNAL.

also that the value of the mobility obtained with the gauze varied markedly with the auxiliary field strength as may be seen below.

Polonium Ions.		Photoelectric Ions.	
Field strength in volt/cm.	Mobility.	Field strength in volt/cm.	Mobility.
1.16	1.74	3.26	1.67
2.40	1.84	6.50	1.87
18.9	2.05	13.10	2.04
38.5	2.21		

This variation of the mobility with the auxiliary field strength might be ascribed to an "ageing" effect in the ions. If the formation of the negative ion from an electron takes an appreciable time, then with the *weak* auxiliary field the mobilities will be measured on more mature ions than they would with the strong field. With the fields used above the ages of the ions in the two cases are about 0.35 second at 1.2 volts/cm. and 0.011 second at 40 volts/cm. A change in the mobility of the *positive* ions with age has been observed by Erikson⁴ and Wahlin⁵ in about 0.01 second. Erikson, however, was unable to detect any such change for the negative ions. Changes in time of from .014 sec. to .073 sec. in crossing the plates with photoelectrically generated ions in some more recent experiments of the writer also showed no change in mobility with age. Finally, if the change in mobility of the ion were due to growth only, then the maximum change observed should be from a mobility of 1.8 cm./sec. to one of 2.18 cm./sec. with the extreme change in fields (*i.e.*, by a factor of 1.21). In another series of measurements from those cited the mobility was found to vary from 1.66 cm. at 1.16 volts/cm. to 2.39 cm./sec. at 97 volts/cm. (*i.e.*, by a factor of 1.44). Thus this explanation is not adequate to account for the phenomenon. An alternative explanation rests on the fact that the mobilities are computed, assuming that the field between the gauze and the plate is given by the potential difference between g and e , and that all the ions start from the plane of the gauze. If, however, owing to the penetration of a strong auxiliary field through the gauze during the negative phase the field strength is greater than that assumed, the mobilities will appear too high. If furthermore, owing to the penetration of the positive phase of the relatively high alternating field through the gauze when the auxiliary field is weak, the ions are cleared from the space near the meshes of the gauze, they will no longer start from the plane of the gauze but from below it.

Thus, the mobilities will appear to be much smaller than they really are. That such conditions actually do exist in experiments using the gauze, and that they can fully account for the magnitude of the effects observed, will be shown in another paper.

The mobilities of the negative ions, as determined by the Franck modification of the Rutherford method, are therefore subject to a grave uncertainty in their absolute value, and one is forced to regard the values obtained with the ions generated directly in the field (Fig. 4a) as being the only correct absolute values that the method is capable of giving. However, the mobilities observed by this method are distinctly above those observed by other methods which, although somewhat discordant among themselves, lie about 1.8 and 1.9 cm./sec. It is impossible to ascribe this difference to any particular cause. There really are only two methods, beside the Rutherford method, which are capable of any great precision. Those are the methods of Zeleny⁶ and Langevin.⁷ In both these methods the ions are generated as a volume ionization by X-rays. They are thus subject to the uncertainties introduced by:

1. The ill-defined region of the ionized volume from which the detected ions come.
2. The non-uniformity of the volume ionization due to the action of the metal walls.
3. The recombination of ions.
4. The distortion of the electrical fields by the intense ionization produced.

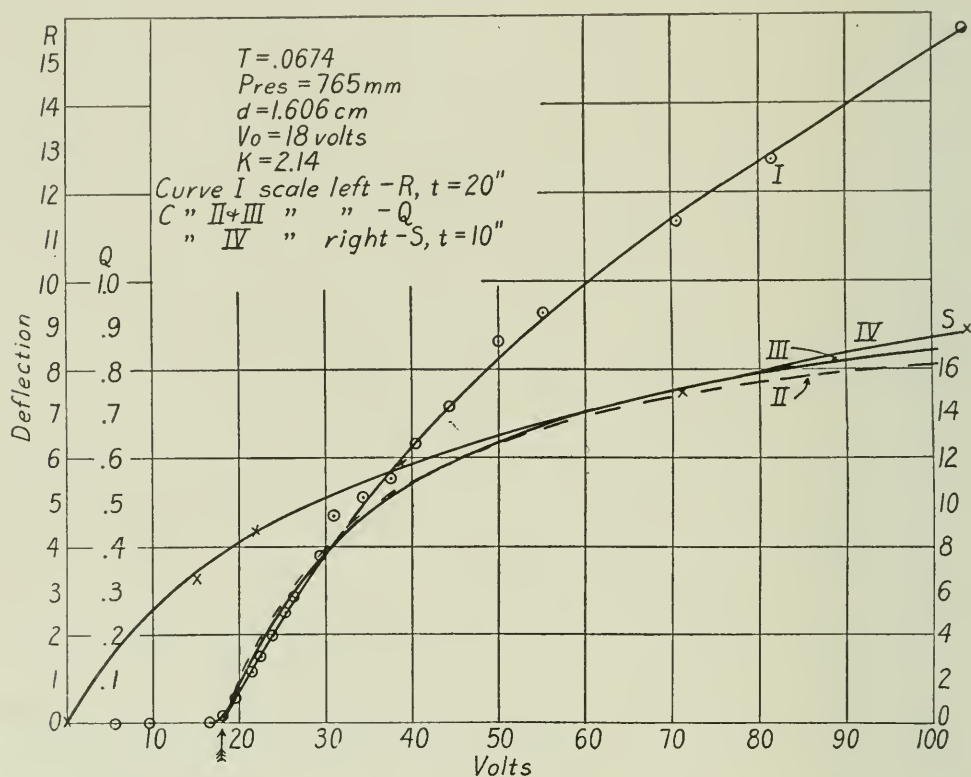
The Zeleny method is furthermore complicated by the unknown conditions of flow of the gas stream and the lack of purity of the large volumes of gases used. While the Langevin method is theoretically free from the complications introduced by the use of X-rays, there may be some inaccuracy in the time intervals between the flash of the X-rays and the closing of the switches, owing to mechanical lags inherent in their operation.

The Rutherford method with photoelectric ions is, however, free from all these uncertainties, for here the ions are liberated from a single plane (*i.e.*, from plate *p*) just at the instant the negative phase begins. There is no recombination and diffusion does not influence the measurement in the short period in which the ions cross the plates. If the plates are parallel, far removed from the walls of the chamber, and not too far apart, the

field is practically uniform, for the density of the photo ions is too small to produce an appreciable effect. The timing produced by the commutator is free from mechanical lags and any error produced by a single phase is averaged out in the hundreds of phases over which the ions are collected.

The mobility observed by this method may, however, be challenged on the ground that since the ion leaves the plate as an

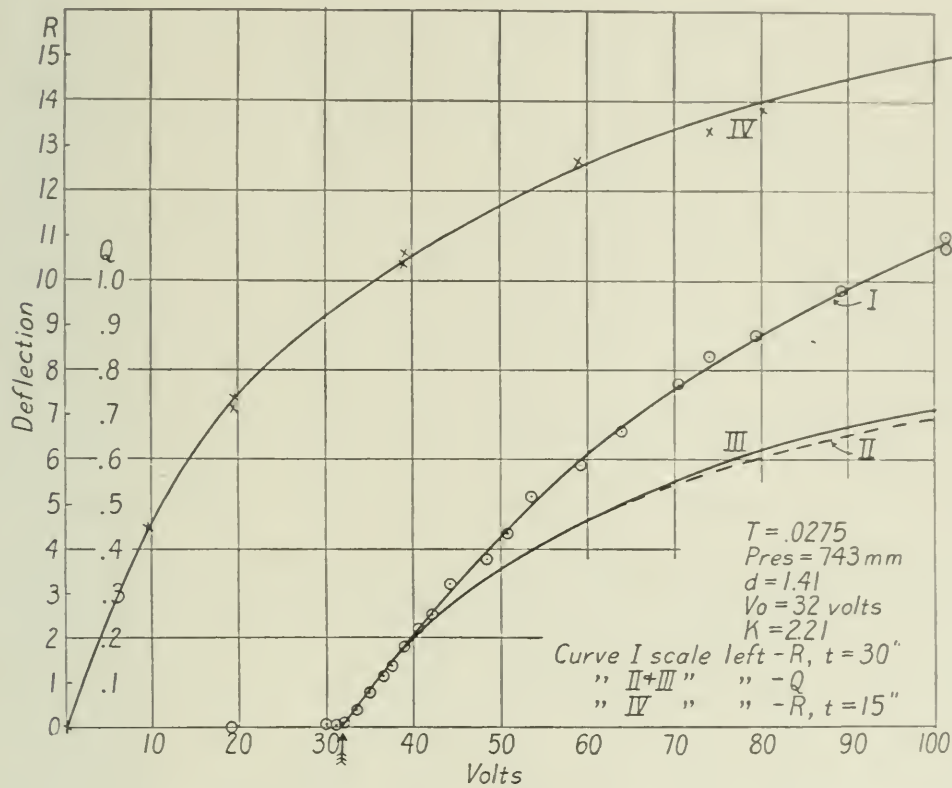
FIG. 1.



electron, the whole process of formation of the ion must occur while it is crossing from p to e , and hence the mobility is not that of a fully formed ion. This formation must first consist in the attachment of an electron to a molecule or an atom. This ion may then further grow by adding on several more molecules. The further growth of the ion seems rather doubtful in view of the fact that Erikson did not observe any change in mobility corresponding to such a growth, and in view of the fact that the electron with its intense field of force shows such a reluctance to attach to a single molecule, that it seems highly doubtful if this molecular ion with its weaker field of force could attach any more molecules. Con-

cerning the distance which the ion travels in the field in its initial electronic stage, we have some definite information. In a later paper the mobilities of electrons in air below 100 mm. will be given. It will there be seen that above this pressure electron mobilities in air are essentially constant and equal to about 1500 cm./sec. The average distance Δ which an electron moves in a field X before attaching to a molecule is then $\Delta = K'nXt$, where n is

FIG. 2.



the average number of impacts with air molecules necessary before an electron can attach ($n = 2 \times 10^5$), K' is the electron mobility, and t is the time an electron spends between impacts. The quantity t may be evaluated from the ratio L/\bar{c} (mean free path divided by the velocity of agitation), which we obtain from the well-known equation of Townsend, $K' = \frac{.815}{300} \frac{e}{m} (L/\bar{c})$. Thus $\Delta = (K')^2 \frac{300mnX}{.815e} = 6.8 \times 10^{-16} (K')^2 \times n$. Under the most extreme experimental conditions used, $x = 50$ volts/cm., and hence $\Delta = 0.15$ cm. As the plate distance here was 1.6 cm. the ions travelled 1 per cent. of this distance as electrons in a very short time. Thus they did not start as ions at the plate p , but at a distance

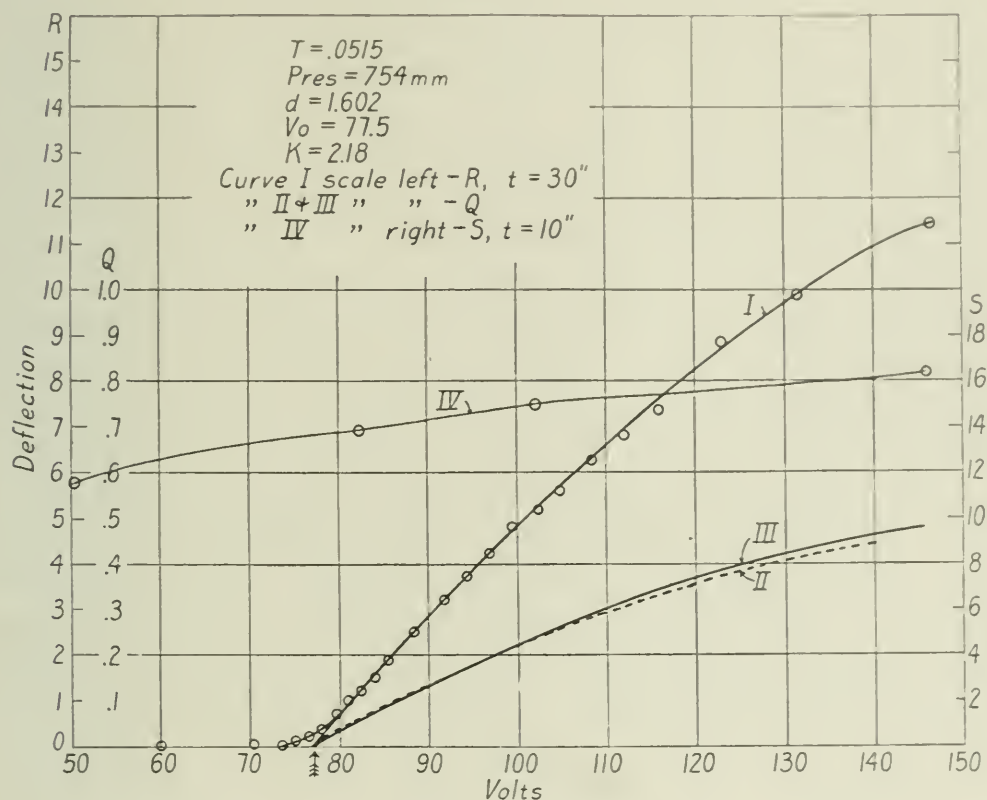
.015 cm. above it. The mobility obtained would therefore be 1 per cent. too high. If the assumption be made that the extrapolation of the electron mobilities at 100 mm. was not justified, and if we assign to the electrons a mobility $K' = \frac{152,000}{21.5 + V}$, which leads to a normal electronic mean free path in air, the error introduced would be at most 1.5 per cent.

The existence of appreciable values of Δ would make themselves evident experimentally by changes in mobility with the value of X , and by the appearance of asymptotic feet at the intercept with the voltage axis. Within the limits of experimental error no certain change of mobility with X could be detected in the measurements with fields between 12 and 50 volts/cm. Below 50 volts/cm. the asymptotic feet were in general absent. At this field strength the feet began to make their appearance to a slight extent (Fig. 3). Finally, as will be shown in a future paper, if we assume that the ions have a *unique mobility constant* and that the ions all start from the level of the plate at the opening of the negative phase (*i.e.*, that $\Delta = 0$) the current to the electrometer at a given voltage V relative to the maximum possible current may be expressed by the relation $I/I_0 = \frac{V - V_0}{V}$; where V_0 is the voltage at which the ions are just able to cross the plates. If the experimental conditions are fulfilled, then the experimental values of I/I_0 should coincide with those computed from the above equation, using the value of V_0 observed. As may be seen in Figs. 1, 2 and 3, curves III (experimental) and II (computed), the curves coincide within the limits of accuracy of the measurements. Although too much significance must not be placed on the coincidence of the curves, the foregoing permits one to conclude that the electronic origin of the ions does not increase the mobility observed by this method by more than 2 per cent. with the field strengths used.

The two ion chambers used in these experiments have been described elsewhere.¹⁰ The plates p and e were housed in large earthed metal cases in which the walls were at least 7 cm. from the plates. Two sources of photo electrons were used. One was a brass plate and the other a speculum metal plate which were illuminated at grazing incidence by the image of a Heræus quartz mercury arc focussed on them by a quartz lens of 4 cm. aperture

and 30 cm. focal length. The plates were insulated from the base by a glass block 5 cm. in diameter and 4 cm. high. Above the plates, suspended from a threaded brass rod, insulated by amber, was the upper plate e , or electrometer plate. By means of a soft iron lug on the brass collar above this plate the plate could be raised or lowered on the threaded brass rod by an electromagnet from outside the housing. This arrangement unfortunately made

FIG. 3.



it difficult to obtain strict parallelism of the plates. The plate distance was measured by a cathetometer which also permitted the lack of parallelism to be determined. When the plates were not parallel, the average distance between them was usually taken. The plates had a diameter of 9.5 cm. in one case and of 10 cm. in the other, and were used with plate distance between 1.4 and 2 cm. only. Thus the fields were fairly uniform. The alternating field came from a two-segment commutator 8 cm. in diameter with the segments separated by a 2 mm. gap of ebonite. This was driven by a motor whose speed could easily be maintained constant within 1 per cent. over periods of two to three hours. The fre-

quency was changed by changing the gear ratio between the commutator shaft and the motor. The P. D. between the plates was furnished by a bank of Columbia dry cells and was read on a Weston D. C. voltmeter. The voltmeter reading was converted to the true potential across the commutator by comparing it with the reading given by a carefully calibrated Kelvin static voltmeter. Owing to the fact that while measurements were being made the P. D. from the commutator acted across the capacity formed by the plates and the capacity of the shielded leads to the electrometer connected in series, the actual P. D. across the plates was less than the applied potential. A correction was made for this by evaluating the capacities involved. The capacity of the leads was very close to 100 cm., while the capacity across the plates varied from 6 cm. to 3 cm. as the distance between the plates was varied from 1 cm. to 2 cm. The correction which lay between 3 per cent. and 6 per cent. was then deducted from the converted voltmeter readings to give the true P. D. acting across the plates. The chambers were closed off without the use of grease or wax and the air used was carefully dried by passing over NaOH, CaCl_2 , two tubes of P_2O_5 , and through a trap cooled to -100°C . by frozen alcohol.

The measurements were taken over a period of two hours' time, the arc being maintained at a constant potential of seventy volts within 1 per cent. during the readings. Under these conditions the photoelectric emission remained essentially constant with the speculum metal plate, while with the brass plate a photoelectric fatigue was observed. This could be corrected for by control reading taken at the beginning and end of the measurement, since the time of each intermediate reading was recorded. In any case this fatigue effect was less than 10 per cent. Each point on a mobility curve was the average of two electrometer readings at a given voltage. Where the two readings differed widely, more readings were taken until a concordant value was reached. Near the critical voltage the readings were taken in 1.5 volt steps. Readings were taken with descending and then ascending values of the potential. At the end of a series of readings the motor was shut down and the measurement of the saturation current was made, the ions being collected over but half the time interval in which they were collected with the alternating current (for with the alternating current the negative phase was on but half the

time). Samples of typical curves obtained are shown in curves I, Figs. 1, 2 and 3. The curves, labelled II and III, are the I/I_0 curves, III being the observed curve, and II being the one calculated from theory, while curves IV are the saturation curves.

As may be seen, the mobility curves are smooth curves making comparatively sharp intercepts with the voltage axis. These curves are typical of all the curves obtained by the writer in the course of four years' work with this type of apparatus. In no case, no matter how carefully the air was dried, has he ever observed the fantastic and irregular mobility curves recently obtained by Nolan⁸ with this method. Curves obtained using a gauze and auxiliary chamber with polonium as a source of ions also failed to show any more irregularities than those shown here. It is the writer's impression, based on long familiarity with this method, that the results of Nolan⁸ and of Haines,⁹ who use the Rutherford method, are irregular because of failure to observe some of the fundamental conditions which must be fulfilled in order that proper results may be obtained. In the experiments of Haines the difficulty is perhaps due to the great plate distances used and the near proximity of the glass walls of his ion chamber to the plates. Thus the fields produced cannot be uniform. Owing to the lack of details in Nolan's description of his apparatus, it is impossible to state the possible cause of his irregularities.

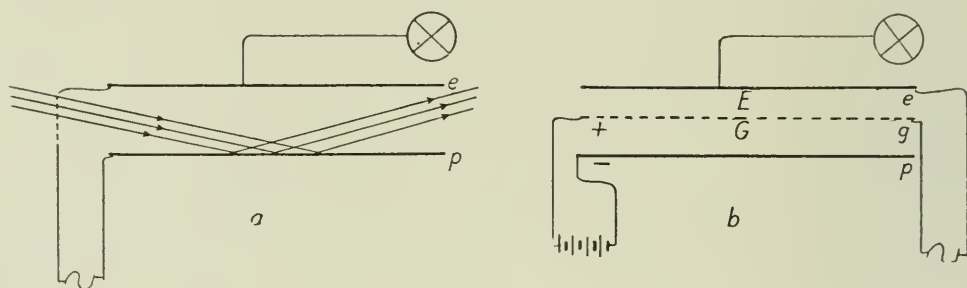
The value of the mobility obtained in fields varying from 12.5 volts to 50 volts/cm., in frequencies varying from 14 cycles per sec. to 75 cycles per sec., and with plate distance lying between 1.4 and 2 cm. at 760 mm. pressure, may be summarized as follows:

Old Ion Chamber Corrected for Lack of Parallelism.	New Ion Chamber Slightly Non-parallel, not Corrected.	New Chamber Quite Parallel.
2.21	2.24	2.14
2.26	2.22	2.18
2.24	2.20	2.14
2.19	2.15	2.23
2.20	2.205 Ave.	2.17
2.19		2.17 Ave.
2.20		
2.20 Ave.		

Weighting the three groups 1, 2 and 3 on the basis of their relative merit, due to parallelism, we get as an average value of

the negative ion mobility the value 2.18 cm./sec. volt/cm. The greatest uncertainties lie in the evaluation of the plate distance where the plates are not quite parallel. This introduces an uncertainty of ± 3 per cent. The estimation of the voltage intercept is not certain to better than .3 volt. At a value of V_0 of 15 volts this makes a possible error of ± 2 per cent. Errors of ± 1 per cent. due to timing, of from 0 to + 2 per cent. on account of the distance gone as an electron and perhaps of ± 2 per cent. in the conversion and correction of the potentials between the plates must also be considered. Taking into account the variety of conditions under which these results were obtained, one may

FIG. 4.



safely place the mobility of the negative ion as $2.18 \pm .04$ cm./sec. volt/cm. in place of the value of 1.8 cm./sec. usually assigned to it.

In conclusion the writer desires to acknowledge his indebtedness to Mr. Lloyd Smede and Mr. R. A. Loveland for their assistance in making some of the measurements.

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NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

APPLE BY-PRODUCTS AS STOCK FOODS.¹

By G. P. Walton and G. L. Bidwell.

[ABSTRACT.]

As only a small part of the moist apple pomace produced each year by cider and vinegar makers can be profitably utilized in the fresh condition or ensiled, its preservation by dehydration is recommended.

Because of its property of absorbing large quantities of water, dried apple pomace is made and used as a source of succulence for the winter feeding of dairy cows. Pound for pound of dry matter consumed, the moistened pomace seemed to be slightly more efficient as a milk producer than corn silage.

Dried apple-pectin pulp, the dried material remaining after the extraction of sugars, pectin, and other water-soluble substances from apple products, seemed to be intermediate between corn silage and beet pulp as a source of succulent feed for cows.

The valuable extractives of apple pomace, sugars and pectin, are utilized as ingredients of food for human beings. All surplus apple pomace should be dehydrated and, together with other suitable apple residues, used as stock food.

SUITABILITY OF VARIOUS SOLVENTS FOR EXTRACTING VANILLA BEANS.²

PART I.

By J. B. Wilson and J. W. Sale.

[ABSTRACT.]

BECAUSE of the restrictions on the use of alcohol which have followed prohibition, and the consequent substitution of other solvents for extraction of flavors, some preliminary work has been done to determine whether or not these alcohol substitutes

* Communicated by the Chief of the Bureau.

¹ Published as *U. S. Dept. Agr. Bul. 1166*, July 26, 1923.

² Published in *Ind. Eng. Chem.*, 15, (Aug., 1923): 782.

produce the same quantity and kind of extracts as those prepared from ethyl alcohol. The investigation was limited to several varieties of vanilla and tonka beans, and the solvents selected were isopropyl alcohol, ether, acetone, and carbon tetrachloride, to be compared with ethyl alcohol. The results show that the alcoholic solvents are much superior from the standpoint of quantity of extraction, the carbon tetrachloride being the poorest in this respect. It is possible, however, that a preliminary extraction with ether or carbon tetrachloride, followed by a weak alcoholic solution, may be found practicable.

PRODUCTION OF SYRUP FROM SWEET POTATOES.³

By H. C. Gore, H. C. Reese, and J. O. Reed.

[ABSTRACT.]

A METHOD for the commercial manufacture of sweet-potato syrup, based on laboratory and plant experimental work, has been developed by the Bureau of Chemistry. From the standpoint of quality, this syrup has possibilities for use as a table syrup, for cooking purposes, and in the manufacture of colored and short-grain candies. For baking purposes it might find a use in dark products, such as ginger snaps. It also has properties which make it suitable for use in blending with other syrup to prevent crystallization.

The commercial possibilities of sweet-potato syrup are limited by the high cost of manufacture under the present method.

EFFECT OF DIALYSIS ON DIRECT CRYSTALLIZATION OF CITRIC ACID FROM LEMON JUICE.⁴

By H. D. Poore.

[ABSTRACT.]

PRELIMINARY experiments using collodion sacs in dialyzing lemon juice, followed by dialysis on a large scale in an osmogene containing collodion-impregnated cloth membranes, gave the following results:

³ Published as *U. S. Dept. Agr. Bul.* 1158, July 3, 1923.

⁴ Published in *Ind. Eng. Chem.*, 15, (Aug., 1923): 773.

(1) The small quantity of colloids present in lemon juice does not affect crystallization, but the ash and other non-acid constituents prevent satisfactory crystallization of concentrated fermented juice.

(2) In the presence of ash and other impurities, needle and leaflet modifications of citric acid crystals are obtained; upon the removal of half of the ash, characteristic citric acid crystals are formed.

(3) At the concentration necessary for crystallization, the mother liquor is so viscous that the crystals cannot be separated.

THE SPECTROPHOTOMETRIC IDENTIFICATION OF DYES.⁵

1—ACID DYES OF THE PATENT BLUE TYPE.

By Walter C. Holmes.

[ABSTRACT.]

THE degree to which the intensity of the absorption of solutions of dyes is modified by variations in concentration, solvent, alkalinity, acidity, and other conditions, depends upon the degree of alteration of the dye in molecular form or aggregation, which, in turn, depends upon constitutional differences. The quantitative measurement of intensity of absorption under such variation in conditions, accordingly, affords spectrophotometric ratios, or constants, which have important diagnostic value for purposes of identification.

In the analytical scheme for the identification of acid blues of the Patent Blue type outlined, such spectrophotometric ratios are employed to supplement the spectroscopic data customarily obtained. A comprehensive table of constants for the identification of the dyes in question is supplied.

Heat of Vaporization of Mercury and of Cadmium.—These constants of nature have been determined by MAYOR F. FOGLER and WORTH H. RODEBUSH, of the University of Illinois (*Jour. Am. Chem. Soc.*, 1923, **45**, 2080–2090). The heat of vaporization of mercury is 14670 ± 50 cal. at 298.1°K. , that of cadmium 25350 ± 100 cal. at 594.1°K. J. S. H.

⁵ Published in *Ind. Eng. Chem.*, **15**, (Aug., 1923): 833.

Recent Contributions of Chemistry to Medicine are discussed by ERNEST H. VOLWILER (*Ind. Eng. Chem.*, 1923, 15, 906-910). Certain dyes, such as acriflavine, mercurochrome and mercuraphen, have found application as bactericides and antiseptics. Acriflavine, also known as trypaflavine, is characterized by the unusual property of more marked bactericidal action in the presence of serum than in its absence. Mercurochrome and mercuraphen are aromatic compounds in which mercury is attached directly to the benzene nucleus. Of the aromatic derivatives of arsenic, mention should be made of arsphenamine, neoarsphenamine, sulpharsphenamine and tryparsamide, which are used to combat diseases produced by certain minute animal parasites known as spirôchetes and trypanosomes. The synthetic hypnotics and sedatives are derived from urethane, the sulphones, ureides, and closely related compounds. Epinephrine or adrenalin, the hormone which is secreted by the suprarenal glands and raises the blood-pressure, has been synthesized on a commercial scale. Thyroxin, the hormone which is secreted by the thyroid and governs the basal metabolism of the body, has been isolated in the pure state. Chaulmoogra oil, which is obtained from the seed of a tropical tree, contains two acids, chaulmoogric and hydnocarpic acids, which are characterized by the presence of a five-membered carbon ring. The esters and salts of these acids are of great value in the treatment of leprosy. J. S. H.

Elimination of Carbon Monoxide from Blood.—The most important factor in the treatment of cases of carbon monoxide poisoning is the early elimination of the carbon monoxide from the blood. R. R. SAYERS and W. P. YANT (*Public Health Reports*, 1923, 38, 2053-2074) have made an exhaustive study of the use of air, oxygen, and a mixture of carbon dioxide and oxygen in the treatment of such poisoning. They draw the following general conclusions: Recovery depends to a great extent upon early elimination of the carbon monoxide from the blood. The rate of elimination depends on the percentage of oxygen in the inspired air and on the rate and depth of respiration. When a person has been gassed to such an extent that 35 or 40 per cent. of the hemoglobin of the blood has combined with carbon monoxide, administration of pure oxygen causes the elimination of the carbon monoxide to proceed four times as rapidly as in normal air. If 8 to 10 per cent. of carbon dioxide be added to the pure oxygen prior to its administration, deep and rapid respiration is produced, and the carbon monoxide is eliminated five to six times as rapidly as in normal air. Every victim of carbon monoxide poisoning not under a physician's care should be caused to breathe oxygen in the purest available form for at least 20 to 45 minutes. It is also recommended that physicians treat the poisoning with the mixture of oxygen and carbon dioxide whenever possible; otherwise they should use pure oxygen. J. S. H.

NOTES FROM THE U. S. BUREAU OF MINES.*

PREPARATION AND DETONATING PROPERTIES OF CYANURIC TRIAZIDE.

By C. A. Taylor and Wm. H. Rinkenbach.

THE detonating compound cyanuric triazide was discovered and patented by Erwin Ott. The Bureau of Mines has determined its properties at request of the Bureau of Ordnance, U. S. Navy.

Pure sodium azide was dissolved in a slight excess of water, and an equimolecular weight of cyanuric chloride was added. The reaction is exothermic, and the temperature rose to about 45° C. The cyanuric chloride was disintegrated as much as possible under the water, and the mixture was allowed to stand for at least twelve hours to insure complete reaction. The solid product was then filtered off and washed with distilled water, and finally dried and weighed. The yield was 90 per cent. of the theoretical, and the product melted at 94° C. The crystals were pure white and very uniform, averaging 0.1 mm. in length. The longest found was 0.3 mm. long and 0.04 mm. in diameter.

Cyanuric triazide is insoluble in water and slightly soluble in cold ethyl alcohol, but it is soluble in acetone, benzene, chloroform, ether, and hot alcohol. It melts at 94° C., and there is decomposition when heated above 100° C. In the molten state it is very sensitive to friction. If heated slowly, it may entirely decompose without detonation, but detonates quickly by flame or sudden heating. The small crystals are more sensitive to impact and friction than mercury fulminate and have detonated when being pressed in a detonator capsule. The large crystals, as may be obtained from fusion or recrystallization, have detonated when broken by a rubber policeman.

Cyanuric triazide is a very efficient detonating agent, but is too sensitive to handle safely in large quantities. It is especially sensitive in the form of large crystals such as may be formed from fusion or recrystallization. It is non-poisonous, but the materials used in its manufacture are irritating and poisonous. Further details are given in Serial 2513, of the bureau.

* Communicated by the Director.

FORMS OF SULPHUR IN STEAMED BLAST-FURNACE COKE.

By John H. Thompson.

RECENT studies at the Pittsburgh Experiment Station of the Bureau of Mines have revealed some interesting facts as to the probable behavior of steamed coke in the blast furnace. Enough small-scale tests were conducted to furnish a check on most of the important deductions, and the conclusions derived therefrom accord with what is already known in regard to the forms of sulphur in coke.

The chief contaminating substances in coke are the free sulphur and the ferrous sulphide. Since these two forms are those which steam most readily attacks, steaming the coke would considerably lessen the contaminating influence of sulphur on the iron. No doubt the removal of these two forms by steam is far greater at the surface of the chunk than at the interior; and since this contamination is a contact phenomenon, this surface removal would be another favorable feature. We should therefore expect steamed coke to give up far less sulphur to the iron than the comparative total sulphur figures would indicate. With a view to checking this point, and also to more nearly duplicate blast furnace conditions, several tests were made on both steamed and unsteamed coke. The coke used contained over 3 per cent. total sulphur. Spongy iron was obtained which contained 0.38 per cent. sulphur, and with the exception of about 5 per cent. of impurities—chiefly carbon—was the same as the sponge iron of the blast furnace. The high-sulphur content made possible a study of the sulphur transfer from the iron into the lime, as well as from the coke into the iron. The same coke was used throughout, the only difference being that in one case it was steamed and in the other unsteamed. This steaming was conducted on chunks of plus $\frac{1}{2}$ inch and minus 1 inch sizes. Neither vacuum nor pressure was used, and the removal was therefore more or less confined to the surface of the chunk.

The results suggest two possible methods for correcting the sulphur trouble in the blast furnace: First, surface sulphur could be removed by some such process as steaming, or hydrogenation; or secondly, it could be prevented from entering the spongy iron at this zone by dipping the coke in some material which would absorb the sulphur more readily than would the iron. Possibly

lime could be used, but whatever the nature of the substance, it should be such that it will not interfere with the proper combustion of the coke at the combustion zone. Further studies along this line would no doubt lead to some interesting discoveries as to the behavior of the sulphur in the blast furnace.

LEACHING NON-SULPHIDE COPPER ORES WITH SULPHUR DIOXIDE.

By Charles E. van Barneveld and Edmund S. Leaver.

THIS bureau has devised a cheap and efficient method for treating the so-called "porphyry" copper ores of the Southwest. These ores generally contain both "sulphide" and "non-sulphide" copper minerals, mixed in such proportions that they can only be satisfactorily treated by a method which will concurrently recover both the sulphide copper and the non-sulphide copper. More than one-half of the copper produced in a recent year in Arizona and New Mexico, amounting in value to \$106,000,000, came from the so-called "porphyry" low-grade deposits.

The sulphur dioxide leaching process, developed by the bureau, in coöperation with the Miami Copper Company and the Arizona Copper Company, is suitable for a wide range of the ores above described. The advantages of leaching with sulphur dioxide are as follows: The plant is compact and not expensive; there are no installation difficulties; power requirements are light. Operation is simple and easily controlled; there are no delicate adjustments or critical points. Percolation difficulties common to leaching are entirely avoided. Perfect contact is assured between the finest ore particles and the reagent; thus, there is excellent utilization of the reagent, which is very cheap. In consequence the process may be extended to ores with so much acid-soluble gangue that they could be treated at a profit by ordinary sulphur-acid leaching. The process is as applicable on a relatively small as on a large scale, and small-scale operation does not necessitate an undue increase in operating cost. Full details are given in Technical Paper 312.

Glucokinin. J. B. COLLIP, of the University of Alberta (*Jour. Biol. Chem.*, 1923, 56, 513-543, 57, 65-78), has discovered a hormone, which he has designated as glucokinin, in the tissues of many plants such as yeast, onion, green leaves of lettuce, wheat and beans.

barley roots and sprouted grain. This hormone is quite similar to insulin, the active principle of the pancreas, since it produces a reduction in the sugar content of the blood when injected into an animal. However, glucokinin acts in a somewhat different manner from insulin; and therefore clinical tests of glucokinin upon diabetic patients have been postponed pending further experiments upon laboratory animals. J. S. H.

Separation and Determination of Potassium and Sodium. G. FREDERICK SMITH, of the University of Illinois (*Jour. Am. Chem. Soc.*, 1923, 45, 2072-2080), has improved the perchlorate method, eliminating the expensive and inefficient extraction with absolute ethyl alcohol, and substituting normal butyl alcohol as a solvent. The new method depends upon the precipitation of potassium perchlorate from its warm aqueous solution in the presence of sodium perchlorate by the slow addition of a relatively large volume of normal butyl alcohol containing from 0.5 to 1.0 per cent. of perchloric acid dihydrate. The solution is boiled with the precipitate for 30 seconds, then cooled to room temperature and filtered through a Gooch or Monroe crucible. The precipitate is washed on the filter, dried for 30 to 60 minutes at a temperature between 150° and 250° C., and weighed as potassium perchlorate.

The sodium is determined in the filtrate by evaporation of the solvent, conversion of the sodium perchlorate into sodium sulphate, and weighing of the latter compound. The sodium may also be determined by difference, weighing the mixed chlorides of sodium and potassium, and then determining the potassium as its perchlorate. J. S. H.

Color Test for Water-soluble B Vitamine. ALADAR JENDRASSIK, of Johns Hopkins University (*Jour. Biol. Chem.*, 1923, 57, 129-138), has studied the behavior of solutions of the water-soluble B or antineuritic vitamine with various reagents. The absence of this vitamine from the diet gives rise to beriberi in man and to polyneuritis in birds. The sole known test for its presence has been a biological test carried out on laboratory animals, especially pigeons and chickens. Jendrassik's results indicate that the vitamine is not an amine, a phenol, an amino-acid, a peptone, or a higher protein derivative. A concentrated aqueous solution containing the vitamine reacts with an aqueous solution of ferric ferricyanide in the presence of acetic acid, acts as a reducing agent, and causes the development of a deep blue color and a bright blue precipitate. This reaction is also given by certain ptomaines, alkaloids, and glucosides; however, none of these compounds would be present in the aqueous extract of a wholesome food. Therefore, if the concentrated aqueous extract of a food yield a positive result in this test, it is presumptive evidence of the presence of water-soluble B vitamine. J. S. H.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

*(Abstract of Proceedings of Stated Meeting held Wednesday,
September 5, 1923.)*

HALL OF THE INSTITUTE,
PHILADELPHIA, September 5, 1923.

MR. W. H. FULWEILER, *in the Chair.*

The following reports were presented for first reading:

No. 2800: Work of William Gaertner in the Design and Manufacture
of Scientific Instruments.

No. 2808: Pneumercator.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, September 12, 1923.)

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BOOK REVIEWS.

GELATIN IN PHOTOGRAPHY. Vol. 1, by S. E. Sheppard, D.Sc. 263 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1923. Price \$2.50 net.

Gelatin in several forms has been a familiar substance from a remote period. The comprehensive discussion of the chemistry and technology of gelatin and glue in the recent book by Bogue affords the student of the subject many interesting data, among which is the suggestion that an Egyptian carving about 3000 years old shows the use of glue as an adhesive, but upon this point there may be doubt. In the interpretation of ancient inscriptions and figures the "will to believe" is sometimes allowed too free play. The work now in hand deals, as the title indicates, solely with the application of gelatin to one line, in which, indeed it has become a most important substance. Gelatin plates and films have made dry-plates of great permanency and sensitiveness possible, and to such qualities is due the immense vogue of photography and its many applications to science, art and amusement. Doctor Sheppard gives a very interesting and instructive summary of the history of the application of gelatin in photography. Many photographers are still living who remember the days of collodion negatives and albumin positives, and can make the contrast in the convenience and many-sided qualities of the modern plate with the older forms. Yet the older methods are not wholly useless.

Lantern slides made with wet-plates are of high quality, and the albumin portrait may in skilful hands serve very well. Even plain paper is not without value in some lines of work.

When we seek to determine the first suggestor of gelatin as a carrier of the sensitive material, we meet the same difficulty as in all similar searches. The question is, what constitutes original invention or discovery? In all departments of science, adumbrations are noted, which will by some be regarded as the first step, by others as having no bearing upon the final result. Dr. R. L. Maddox, of England, is usually credited with the invention of the dry-plate yet he did not develop his work to satisfactory commercial condition, and it was left to others to carry further the procedure. Maddox, in 1871, used a gelatin-bromide emulsion. It appears, as is so often the case in science, that the success of the gelatin-bromide emulsion depended on two independent conditions. As early as 1862, two investigators had independently discovered that alkaline pyro development was successful with gelatin plates. Such developer applied to collodion coatings was not successful. A great step in the preparation of the gelatin plates was the discovery of the advantage of removing all the soluble salts from the emulsion. This is in marked contrast to the old collodion process, in which the presence of the excess of silver nitrate was necessary, the image being indeed formed from this nitrate, and not from the decomposition of the silver halide upon which the so-called latent image is formed. Here, again, two independent workers made the discovery. It is not necessary to set forth in further detail the incidents of the history of the modern process. They are set forth in a very satisfactory manner in the book. The history of any such procedure is always of value, both as showing the difficulties of the matter, and as also the direction in which research should be pursued. It is always important to bear in mind that even the most implicitly received statements and doctrines may be erroneous, and it is well to test out older data before proceeding to investigate the unknown. It is worthy of note that the present high development of the film photograph, especially in rapid photography and motion picture work, involves inventive talent and research in several lines not in any way connected with photography. The production of flexible, transparent nitrocellulose film and the invention of powerful illuminants are due to other interests than picture making, but have one of their most extensive uses in such work.

The whole process of making commercial gelatins and the general properties thereof form the subject of one chapter, followed by descriptions of the analytic and constitutional chemistry, and the physical testing of gelatin. A comprehensive bibliography and two good indexes occupy the later pages of the book.

The work is a valuable contribution to a highly important field of applied science. Photography has entered into so many phases of life that anything authoritative about it or the materials used in it will be welcome. Printing has been termed the art preservative of all arts, and photography is rapidly displacing ordinary printing in many fields. Gibbon, in speaking of the destruction of manuscripts at the taking of Constantinople by the Turks in 1453, said that fortunately the "mechanics of a German town had invented

an art that enables literature to defy the ravages of time and barbarism." Photography goes further, for it preserves to us the scenes and incidents of actual life. The Eastman Company is doing most excellent work in its research laboratories and publishing departments.

HENRY LEFFMANN.

CHEMISTRY, INORGANIC AND ORGANIC, WITH EXPERIMENTS. By Charles Loudon Bloxam. Eleventh edition, revised by Arthur G. Bloxam, F.I.C., and S. Judd Lewis, D.Sc., F.I.C. 832 pages, including index, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. Price \$9.

Bloxam's Chemistry appeared first in 1867. Though too large for a student's textbook—a field in which the works of Fownes and Silliman were prominent—Bloxam's book was very serviceable for teachers and was widely approved. The author was a teacher as well as research chemist and produced therefore a manual which was comprehensive. His connection with one of the British military schools gave him special interest in the chemistry of explosives, and the book devoted rather more attention to such subjects than was usual in the manuals of that day. Of course, the subject was then much simpler. Although several of the high nitro-explosives were known, the applications of them were not as wide, and the problems of asphyxiating gases and gas masks have of late years brought chemistry into wide and weighty relations to the nations as well as to certain industries. Bloxam was always somewhat conservative in his attitude to theories in chemistry, and preferred to set before the student a considerable amount of what is commonly known as "practical" chemistry before taking up many of the principles. The present edition follows this plan. Nearly three hundred pages are given, largely to elaborate description of experiments, before the general principles of chemistry are set forth. The aliphatic and cyclic hydrocarbons are considered in the same section, a plan which the editors state has met with approval by some and disfavor with others. The matter is probably of no great importance.

The book contains a large amount of information and has been brought up to date on most points. An exasperating condition is the retention of a considerable amount of very old and quite antiquated matter, which simply serves to occupy valuable space. This criticism applies to the illustrations as well as to the text. Many cuts are used which are from the first edition. One of the most astonishing instances of this lack of elision is on pages 16 and 17, in the discussion of the decomposition of water. It is, indeed, not explained that the ordinary electrolytic experiment with water acidulated with sulphuric acid is really a decomposition of the acid and not of the water, but that perhaps is of minor importance, as the water is affected in the secondary reaction, but the suggestion that Grove's cell be used certainly seems strange. Grove's cell went out of use a half century ago, by the invention of cheaper and better methods, and with platinum at about \$3 a gram, it is wholly out of the question. The apparatus shown for obtaining hydrogen and oxygen by acting on dilute sulphuric acid with an electric current is a form that is quite out of date. Even some of the cuts, apparently drawn for the recent editions, are lacking

in contemporaneousness. Such is the sketch on page 30 of an apparatus for distilling water. Such apparatus is not now used either on the large scale or in the analytical laboratory. It seems also a waste of space to give some of the methods of making oxygen that are no longer used.

These antiquated procedures and apparatus detract somewhat from the merit of the book, and certainly, as noted above, occupy space that could be devoted to better uses. The price seems rather high for a volume of this size, but it is excellently printed and a large amount of information is presented in a clear and understandable form. It is certainly a convenient and useful work of reference for teachers and advanced students.

HENRY LEFFMANN.

THE OFFICE OF THE CHIEF OF ENGINEERS OF THE ARMY. By W. Stull Holt. xii-166 pages, 8vo. The Johns Hopkins Press, Baltimore, 1923. Price \$1 net.

This is one of the series of publications of the Institute for Government Research, an association of citizens for coöperating with public officials in the scientific study of government with a view of promoting efficiency and economy therein. That there is need for such studies is evidenced everywhere and always. Even in private affairs there is much need of scientific study of methods. The popular idea that all private institutions are well-managed and all public institutions badly managed is not correct. The present work relates to the work of U. S. Army engineers, a corps which has a long history, for the Continental Congress on June 16, 1775, one day before the battle of Bunker Hill was fought, authorized the appointment of certain army engineers, and later authorized General Washington to organize a corps. Several French engineers were appointed under this authority. Army officers have had a great deal to do with public works of a non-military character. The question of internal improvements, especially in the vast districts that were acquired by the Louisiana purchase, and the later extension of the Mexican treaty and the Gadsden purchase, brought complicated problems of river and harbor improvements, and road construction into prominence. A considerable amount of political and economic antagonism arose in and out of Congress. The eastern, well-settled and mostly industrial and commercial sections were opposed to spending money on the internal improvements of the West. The eastern sections wanted high prices for public lands in order to deter emigration of labor, and tariff on manufactures. The western sections wanted low prices for public lands and rather low tariffs. National support for such improvements developed but slowly until the close of the war between the States, when the federal power had greatly increased and the western populations had secured a great influence. The story of these struggles is told in an introductory chapter, and is well worth reading by those who are interested in the progress of the United States towards a "more perfect union," and to a united economic effort. The historical portion occupies nearly half the book. Data on the activities of the corps then follow, after which statistical data are given.

HENRY LEFFMANN.

PHYSICS IN INDUSTRY. Lectures delivered before the Institute of Physics. 39 pages, 8vo. New York, Oxford University Press, American Branch, 1923. Price 85 cents.

This volume contains the text of three lectures, respectively, "Physics and Engineering Science," by Prof. Archibald Barr; "The Physicist in Engineering Science," by Sir James Alfred Ewing, and "The Physicist in Electrical Engineering," by Clifford C. Patterson. These lectures are initiative to a course which the Institute of Physics has decided to offer, both for the purpose of interesting the public in general as to the value of research and pure science in aiding practical applications, and also as a guide to students, suggesting lines of usefulness in their studies. Undoubtedly there has been in most great nations an indifference to the value of abstract research. English-speaking peoples have been probably the greatest offenders in this line. Matters have improved somewhat of late years, largely through the severe lessons taught by the war, but much still remains to be done. It is claimed in the preface of this book that there is work to be done for the industries that only physicists can do. This is true, but the claim must not allow us to overlook the fact that there is also much that the chemist alone can do. It is not difficult to name discoveries that when made have seemed remote from practical value and yet have been the initiative of highly useful inventions. The lectures are a useful contribution to the general propaganda in the cause of greater public support of research.

HENRY LEFFMANN.

THE CHEMICAL ENGINEERING CATALOG. Eighth Annual Edition, 1049 pages, 4to, flexible cover. New York, The Chemical Catalog Company, 1923. Price \$10.

Notice was made of the seventh edition in the issue of this JOURNAL in November, 1922. The present issue covers the same ground and is made up in the same way. The method of leasing the volume for a comparatively small sum is still followed, but the book may be purchased outright for the sum noted above. It is the official standard work of reference for chemical engineers, works managers, purchasing agents and many others who are connected with the now extensive development of the chemical industries and especially those that buy equipment and materials for use in chemical processes. The volume is prepared under the supervision of a joint committee of the American Chemical Society, the Society of Chemical Industry and the American Institute of Chemical Engineers, but the members thereof have no financial interest in the work. The book consists in the main in a compendium of many catalogues and is intended to inform the purchaser rather than advertise the wares. The supervising committee takes care that general claims, exaggerated statements and display material are excluded, and endeavors to secure the presentation of precise data, including specific uses or adaptation of the equipment or materials. The extensive development of chemical industries in this country is one of the encouraging conditions, tending as it does to render us independent of other nations, and thus able to "go it alone" if war or other catastrophe occurs. The lesson given during the late war does not seem to have

been fully learned by the American people, who are apparently allowing some of the important key industries, especially that of nitrogen fixation, to lapse.

The preface contains a great deal of information concerning the distribution of the work. By furnishing to all firms that carry space a printed list giving the names and addresses of those to whom the book is distributed the value of the compilation is greatly increased. The book is really a wonderful compilation. It is, of course, abundantly illustrated, and being printed on fine paper with clear type and with excellent taste in the display portions, it constitutes a most interesting demonstration of the high degree of efficiency and extensive specialization that the mechanical and chemical interests have undergone. The binding is flexible and permits the book to lie open flat at any page.

HENRY LEFFMANN.

LE MAZOUT. Par E. Davin. 96 pages, 12mo. Paris, A. D. Cillard, editeur, 1923. Price 22 Francs.

Mazout is a Russian word meaning heavy petroleum, that is, fuel-oil. Why such a barbarous term should be introduced into science is difficult to understand, but it seems to have been adopted by French engineers. The pamphlet contains much information on the nature, testing and uses of fuel-oil. The subject is one of great and growing importance, and has, indeed, become one of the most critical problems in international relations. The constantly increasing price of coal and liability of the industry to interruption from strikes have turned the attention of all active nations to the substitution of oil for solid fuel. The saving of labor is immense. In a recent account of the installation of a sea-water distillation apparatus in Chile, it was stated that the substitution of oil for coal enabled the operation to be carried on with two men where eight had been needed when coal was used.

Power engineers of all types will be much interested in this pamphlet, both theoretical and practical data being included. The author states that the first use of petroleum in boiler-firing was by a Russian engineer, Spakowski, in 1867. This was probably the use in locomotives and steamers in the Baku region, where the Russian heavy oil is obtained. Considerable space is given to the recently suggested, so-called "colloidal," fuels, that is, heavy combustible oils containing suspensions of finely powdered solid fuels. Notes of experiments in this field are given from American sources. A U. S. destroyer was fired by a mixture of 31 per cent. of Pocahontas coal and the fuel-oil commonly used in the U. S. Marine. A small quantity of an emulsifying agent had been added to maintain the mixture. There seems to be great promise of useful, economical results along this line.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 166, The Aerodynamic Plane Table. By A. F. Zahm. 11 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

For the accurate and expeditious geometrical measurement of models in an aerodynamic laboratory, and for miscellaneous truing operations, there is frequent need for a specially equipped plane table. For example, one may

have to measure truly to 0.001 inch the offsets of an airfoil at many parts of its surface. Or the offsets of a strut, airship hull, or other carefully formed figure may require exact calipering. Again, a complete airplane model may have to be adjusted for correct incidence at all parts of its surfaces or verified in those parts for conformance to specifications. Such work, if but occasional, may be done on a planing or milling machine; but if frequent justifies the provision of a special table. For this reason, it was found desirable in 1918 to make the table described in this report and to equip it with such gauges and measures as the work should require.

Report No. 169, *The Effect of Airfoil Thickness and Plan Form on Lateral Control*. By H. I. Hoot. 11 pages, illustrations, quarto. Washington, Government Printing Office, 1923.

Tests for the purpose of determining the effectiveness of ailerons were made on six model airfoils in the No. 1 wind tunnel of the National Advisory Committee for Aeronautics. The method consisted in measuring the rolling moments and aileron moments in the ordinary way. In addition to this the wing was allowed to spin freely about an axis in the direction of the air flow and the angular velocity measured.

The results show that the thickness of the airfoil has very little effect on either the rolling moment or the hinge moment, but that the tapering in plan form somewhat decreases the rolling moment and hinge moment, although the resulting efficiency is somewhat higher for the tapered wings. The airfoil tapered in plan form, however, shows practically no falling off in the rolling moment at the critical angle of attack, whereas the wings of rectangular plan form show a marked dropping off in the rolling moment at this point. This indicates that it is possible to obtain good lateral control with small ailerons at low speeds if the plan form is tapered. The rotational speed of the different airfoils is practically the same for all of the sections tested.

PUBLICATIONS RECEIVED.

Chemistry, Inorganic and Organic, with Experiments. By Charles Loudon Bloxam. Eleventh edition, revised by Arthur G. Bloxam, F.I.C., and S. Judd Lewis, D.Sc. 832 pages, illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. Price \$9.

Heat and Energy. By D. R. Pye. Clarendon Science Series. 211 pages, illustrations, 12mo. Oxford, Clarendon Press; New York, Oxford University Press, 1923. Price \$1.70.

Gelatin in Photography. Vol. I, by S. E. Sheppard, D.Sc. 263 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1923. Price \$2.50.

Biomathematics, being the Principles of Mathematics for Students of Biological Science. By W. M. Feldman. Introduction by Sir William M. Bayliss. 398 pages, illustrations, 12mo. London, Charles Griffin and Company; Philadelphia, J. B. Lippincott Company, 1923.

Mineral Valuation. By Henry Louis. 281 pages, illustrations, 8vo. London, Charles Griffin and Company; Philadelphia, J. B. Lippincott Company, 1923.

Institute for Government Research. Service Monographs of the United States Government, No. 27. The Office of the Chief of Engineers of the Army. Its non-military history, activities, and organization, by W. Stull Holt. 166 pages, 8vo. Baltimore, The Johns Hopkins Press, 1923. Price \$1.

La Tension de Vapeur des Mélanges de Liquides. L'Azéotropisme par Maurice Lecat. Première partie, Données expérimentales. Bibliographie. 319 pages, 8vo. Gand, Belgium, Ad. Hoste, 1918.

Carènes de Formes Nuisibles ou Favorables a leurs Grandes Vitesses; et Résistances de l'Eau a leur Translation. Par M. le vice-amiral F. E. Fournier. 27 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price 3 Francs 50.

Probité Scientifique. Par Maurice Lecat. 24 pages, 8vo. Louvain, Author, 1923.

Bibliographie des Séries Trigonométriques. Avec une appendice sur le calcul des variations par Maurice Lecat. 169 pages, 8vo. Louvain, Author, 1921.

Bibliographie du Calcul des Variations Depuis les Origines Jusqu'à 1913. Par Maurice Lecat. 2 vols., 8vo. Gand, Belgium, Ad. Hoste, 1913, 1916. Price 8 Francs 50.

Physics in Industry. Lectures delivered before the Institute of Physics by Archibald Barr, Sir James Alfred Ewing, and Clifford C. Patterson, with a foreword by Sir J. J. Thomson. 59 pages, 8vo. London, Henry Frowde, 1923. Price 85 cents.

Le Masout. Par E. Davin. 96 pages, illustrations, 12mo. Paris, A. D. Cillard, 1923. Price 22 Francs.

Canada Department of Mines, Mines Branch. Silica in Canada, Its Occurrence, Exploitation and Uses. Part I, Eastern Canada, by L. Heber Cole. 126 pages, illustrations, plates, maps, 8vo. Ottawa, Government Printing Bureau, 1923.

National Advisory Committee for Aeronautics: Report No. 161, The Distribution of Lift over Wing Tips and Ailerons, by David L. Bacon. 23 pages, illustrations, quarto. Technical Notes, No. 153, Flight Characteristics, by Captain Student. 8 pages, quarto. No. 154, An Instrument for Recording the Position of Airplane Control Surfaces, by K. M. Ronan. 4 pages, photograph, quarto. No. 155, Regulations Governing the Issuance of Certificates of Airworthiness of Aircraft in France. 46 pages, quarto. No. 156, The N.A.C.A. Recording Tachometer and Angle of Attack Recorder, by H. J. E. Reid. 3 pages, photograph, quarto. Washington, Committee, 1923.

Melting Point of Ice on the Absolute Scale.—A recalculation of the melting point of ice on the absolute temperature scale by LEIGHTON B. SMITH and ROBERT S. TAYLOR, of the Massachusetts Institute of Technology (*Jour. Am. Chem. Soc.*, 1923, **45**, 2124–2128), gives the value 273.13° .
J. S. H.

CURRENT TOPICS.

A Radio-acoustic Method of Locating Positions at Sea. A. B. WOOD and H. E. BROWNE. (*Proc. Phys. Soc.*, April 15, 1923.)—A charge of 9 ounces of explosive is fired in water and at the same time a dash is sent by wireless telegraphy. The two waves arrive at different times at four stations in the sea of which the location is known. The speed of the wireless wave is so great that it may be regarded as arriving simultaneously at all points within a radius of a few hundred miles. The arrival of the explosion wave is noted by a hydrophone and the resulting current is transmitted to one string of an Einthoven galvanometer on shore. This instrument has three additional strings for as many more hydrophones, a string for a time-recording device and still another for the recording of the arrival of the dash. The speed of the wave in water is accurately known in its dependence on temperature and salinity. The product of this speed by the number of seconds required for the wave to travel to the hydrophone from its source gives the distance of the source from the hydrophone. The source is, therefore, located anywhere on a circle drawn around the hydrophone as a centre with this product as a radius. From the data derived from a second hydrophone the source will be located on a second circle. It must in consequence be at one of the two points where two circles in general intersect. The third hydrophone fixes definitely the position of the source. The location of a vessel can be furnished to it within ten minutes of the time when request was made for a "fix." In misty weather with heavy seas the locations obtained by this method were more accurate than those got by the navigating officer through the use of ordinary methods. "The R/A method possesses the very great advantage of being equally accurate and reliable, day and night, at all seasons of the year and under all weather conditions—whereas directional W/T locations are often open to doubt, peculiar errors of several degrees in bearing being of frequent occurrence."

G. F. S.

A Supposed Relationship between Sun-spot Frequency and the Potential Gradient of Atmospheric Electricity. C. CHREE. (*Proc. Phys. Soc.*, April 15, 1923.)—From a consideration of the observations made at the Ebro Observatory, Spain, Dr. L. A. Bauer has drawn the conclusion "that both the range of the diurnal inequality of atmospheric electricity potential gradient and the mean value of the element for the year increase and diminish with sun-spot frequency." At Kew a Kelvin water-dropping electrograph has been in operation since 1862. An examination of the data furnished by it

in a general way is confirmatory of Doctor Bauer's conclusion yet "one would like to feel quite sure that there is no reasonable explanation of a more local nature than sun spots for the phenomena."

"It may be pointed out that if the mean annual gradient of potential waxes and wanes all over the earth with sun-spot frequency, so also must the earth's total negative charge."

At the close of the paper Dr. D. Owen asked whether the electric fields observed extended only between the surface (of the earth) and the upper atmosphere. The speaker replied, "Observations of potential gradient made from balloons in fine weather have shown a rapid decline in the gradient with height above the ground. The inference is that the lower layers of the atmosphere contain a charge opposite in sign to that of the earth's surface. Balloon observations have not, so far as I know, ever shown an actual reduction to zero in the potential gradient. But the natural inference from the somewhat limited data available is that under normal conditions the lowest 10 km. of the atmosphere contain a charge opposite in sign to that on the earth's surface and making at least a close approach to equality with it."

G. F. S.

Effect of Germanium Dioxide upon the Blood.—Germanium dioxide has been used in the treatment of certain types of anæmia. JOHN HUGHES MÜLLER and MIRIAM STEWART ISZARD, of the University of Pennsylvania (*Jour. Metabolic Research*, 1923, 3, 181-199), have made an exhaustive study of the effect of germanium dioxide upon the blood. A concentration of 0.014 per cent. of germanium dioxide represents the approximate saturation capacity of the blood for that compound; therefore, the maximum effect is produced in a person of average weight by administration of 0.8 to 1.0 gram of the dioxide. In venous blood, the germanium is localized in the cellular elements rather than in the plasma. In oxygenated or arterial blood, the germanium occurs in greater quantity in the plasma than in the cells; this blood yields an absorption spectrum which does not differ noticeably from that of normal oxyhemoglobin. However, reduced or venous blood containing germanium yields a characteristic absorption spectrum, which appears upon exposure of the oxygenated blood to the action of reduced pressure, carbon dioxide, or certain oxygen-consuming bacteria. Apparently when germanium dioxide is injected into the system, it is reduced in the tissues to germanous oxide which then combines with the hemoglobin of the red blood-cells and appears in that form in the venous blood. On oxygenation of the blood in the lungs, the germanous oxide is oxidized to the dioxide, which is non-volatile and remains in solution in the plasma or liquid portion of the blood. In this form, it returns to the tissues with the arterial blood. Here reduction again occurs; and the entire cycle is repeated. Hence the germanium derivatives may function as oxygen carriers in the blood

stream. Germanium dioxide also exerts a specific erythropoietic action, that is, causes the animal organism to produce erythrocytes or red blood-corpuscles.

J. S. H.

The Mechanism of Soaring and the Morphology of Soaring Birds. C. NORDMANN. (*Comptes Rendus*, Aug. 20, 1923.)—In soaring both propulsion and sustentation need to be explained. "It is easy to show by elementary considerations that by arranging its wings properly the bird finds in the wind a component urging it forward. . . . The problem of sustentation in soaring is, on the other hand, still in suspense." The theory, proposed by Mouillard and developed by Langley, that the bird is kept up by utilizing each gust in a series, is discussed and rejected as unsatisfactory. The author produces the following theory for consideration, that the angle of attack of the bird is not always positive, as has hitherto been assumed. It is positive when the gust causes a motion of the bird into the wind and negative when the wind overtakes the bird. In both cases there would be an upward component, supporting the weight of the bird.

This at once makes clear certain actions of soaring birds that could not be explained by the former theory such as the fact that they progress continuously upward both in straight and in curved flight. Further, an examination of the structure of soaring birds discloses that it is just such as would be needed did they have the ability to make the same adjustment of angle to a wind coming from the rear as to a wind from the front. Furthermore the location of the centre of gravity of the bird and the position of the terminal pinions of the wing in soaring cause the adjustment of the angle of attack to be automatic.

G. F. S.

Work of the Physikalisch-Technische Reichsanstalt for 1922. (*Zeit. f. Instrumentenk.*, March, 1923.)—The President, Professor Warburg, retired in March, 1922, and was succeeded by Professor Nernst.

Early in the report is found a statement of the difficulty experienced in getting magazines. Only in America was it possible to arrange exchanges with satisfaction. The *Philosophical Magazine* was furnished gratis by a professor in Upsala. The *Electrician* could not be had at all on account of the high price as expressed in worthless currency.

To show the high value of the work performed nothing is needed beyond an enumeration of the subjects of investigation, but this in itself would fill too large a space. Let these suffice the Balmer series of hydrogen, examination of radioactive preparations, the melting point of platinum, testing of 8962 non-clinical mercury thermometers, diffusion of helium through glass, metallic crystals, high frequency telephone, photo-chemistry.

G. F. S.

The Electrification Produced by the Pulverization of Aqueous Solutions. J. J. NOLAN and REV. H. V. GILL. (*Phil. Mag.*, Aug., 1923.)—"The liquid is sprayed in a horizontal direction from a metal sprayer driven by air under pressure. The drops fall into an insulated metal tray. This, together with the sprayer itself, which is also insulated, is connected to a Dolezalek electrometer which measures the charge. The electrometer therefore records the charge on the water due to the electrical separation at the water-air surface, the charge of the opposite sign being carried off in the air as an excess of ions of one sign." In a previous paper one of the authors examined the electrical charges produced when water of differing degrees of purity was broken into smaller portions in contact with air. "Considered in connection with Simpson's theory of thunderstorm electricity, the magnitudes of charge observed showed that if a moderate degree of purity were attributed to the rain-drops in a thunderstorm, the breaking of the drops in the manner supposed by Simpson would produce sufficient separation of electricity to account for the observed effects."

The method of the present paper was to vary the concentration of the solutions tested while the pressure of the sprayer and consequently the degree of pulverization was kept constant. "The substances most likely to be present in rain in the free atmosphere are nitrates, sodium chloride from evaporated sea spray, hydrogen peroxide and dissolved gases such as ammonia, carbon dioxide, oxygen, and nitrogen. It may be stated at once that, judging from their effect when added to distilled water, these substances, with the single exception of sodium chloride, will not seriously affect the charge developed when a rain-drop is broken." When NH_3 is present to the amount of .5 gram per litre of water, that is, in a proportion about 1000 times as great as that occurring in country districts, then the electrical charge manifesting itself drops to 1 per cent. of that of pure water. "If Simpson's theory of thunderstorms is correct, it would seem that if ammonia could be introduced into the thunder-cloud in sufficient quantity to form with the rain-drops a solution of this strength (or even one-tenth of this strength) the development of a thunderstorm would be seriously impeded. This is an experiment which is perhaps within the bounds of possibility."

It was only after long search that the authors succeeded in obtaining negative charges from the breaking up of solutions of sodium chloride. Finally such charges were got from a high degree of pulverization. The general conclusions of the paper are these:

(1) "Inorganic salts in increasing concentration diminish the positive charge when water is broken."

(2) "Non-electrolytes do not affect the development of charge."

(3) "A group of substances shown by Lewis to give abnormal adsorption effects have a great influence on the sign and magnitude of the charge at very low concentrations."

G. F. S.

On the Changes in Iron and Steel at Temperatures Below 280° C. F. C. THOMPSON and EDWIN WHITEHEAD. (*Proc. Roy. Soc., A* 218.)—The change of electrical resistance produced by a rise of temperature was studied for pure iron, mild steel, high carbon steel and white pig iron. When the change per degree is plotted against temperature a series of maxima and minima discloses itself, the first of which is not much above room temperature. The general form of the curves is that of a succession of written u's. Between 20° and 260° C. all but the pig iron show nine cusps. It has ten. An examination of the thermoelectric power confirms the evidence previously obtained. "Iron shows abnormalities of the rates of increase of electrical resistance and electrical potential against platinum at well-marked temperatures. Below 280° C. these temperatures are $55, 100, 120, 140, 220$ and 245° C. Of these those at 120 and 220° C. are the most important. It is difficult to believe that these can be of the nature of allotropic changes, and for the time the explanation must be taken as unknown. Under the same conditions carbide of iron possesses two well-marked points at 160 and 200° C." G. F. S.

Insulin.—The pancreas produces two secretions, an external and an internal. The external secretion is a digestive fluid and passes through a duct into the intestine where it exerts a digestive action on starches, fats and proteins. The internal secretion is insulin; it is produced by the regions of the pancreas known as the islands of Langerhans, passes directly into the blood-stream, and governs the metabolism of the sugar which has been absorbed from the intestine. Diabetes mellitus is due to the failure of the islands of Langerhans to produce insulin. The sugar content of the blood then becomes excessively high, and sugar is present in the urine. Banting, of the University of Toronto, has succeeded in preparing insulin from the pancreas of slaughter-house animals by a process of alcoholic extraction. The insulin is administered by injection, and has been used with marked success in the treatment of diabetes. However, treatment must be continued indefinitely. Great care must be exercised with respect to the dosage, especially to avoid an overdose. Therefore its use should be under the control of a physician. A summary of our present knowledge of insulin is given by R. M. WILSON (*Science Progress*, 1923, 17, 585-587). J. S. H.

The Crystal Structure of Various Heusler Alloys by the Use of X-rays. J. F. T. YOUNG. (*Phil. Mag.*, Aug., 1923.)—At present, in spite of the fine work of Langevin, Pierre Weiss, Gans and the Comptons, there is no theory of magnetism that is entirely satisfactory and the nature of the ultimate magnetic particle remains a matter of debate. This paper presents the results of an investigation of the Heusler alloys, discovered in 1903. They contain the two paramag-

netic metals, manganese and aluminum, and the diamagnetic metal, copper, and some of them have magnetic qualities similar to those of soft iron. Since such alloys are quite strongly magnetic, though built up of metals, no one of which is anything but weakly paramagnetic or diamagnetic, they might well furnish some clue to the type of arrangement that causes magnetic properties. With this in view "a systematic crystal analysis of definite Heusler alloys in different conditions was undertaken, using X-ray methods." In no case did the photographs of the diffraction patterns of the two alloys investigated show any trace of the lines characteristic of the three constituent metals. The interpretation of the figures led to attributing to the magnetically weaker the crystal structure of a face-centred cube and to the stronger that of a combination of this same face-centred cube with a body-centred cube. Just this same difference of structure had been previously found to exist between a nickel steel in its non-magnetic state and in its magnetic state. "The superposition of a magnetic field of 3500 gauss did not alter the crystal form of the alloys or make any noticeable change in the relative intensities of reflection from the different crystal planes, indicating no change in orientation of the crystal unit."

G. F. S.

Stability of Sodium Thiosulphate Solutions.—Since standard solutions of sodium thiosulphate are extensively used in volumetric analysis, the stability of these solutions is a matter of great importance. MARTIN KILPATRICK, JR., and MARY L. KILPATRICK, of Vassar College (*Jour. Am. Chem. Soc.*, 1923, **45**, 2132-2135), have studied the stability of several one-hundredth normal solutions of this salt over a period of eight months. Freshly boiled redistilled water yielded a solution which was more permanent than those prepared with laboratory distilled water, ordinary redistilled water, and redistilled water through which air free from carbon dioxide had been bubbled. The stability of the solution was influenced but little by carbon dioxide, oxygen, and dilute sodium hydroxide. Decomposition of the solution was caused by the action of bacteria.

J. S. H.



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THE CATHODE-RAY OSCILLOGRAPH AND ITS APPLICATION TO THE EXACT MEASUREMENT OF EXPLOSION PRESSURES, POTENTIAL CHANGES IN VACUUM TUBES AND HIGH TENSION MAGNETOS.*

BY

DAVID A. KEYS, Ph.D.

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I. INTRODUCTION.

IN MANY physical and engineering problems it is necessary to possess an instrument which will record accurately very rapid variations in electrical potential. For such a purpose any device possessing a recording system with appreciable mass would not be suitable owing to the inertia of its moving parts. The ordinary Braun tube, in which a beam of electrons passes between two deflecting charged plates and falls on a fluorescent screen, is satisfactory for those cases in which the electrical variations are periodic and go through the same cycle many times. The beam of cathode rays will traverse the same path each cycle, and the fluorescent curve traced on the screen may be photographed with an ordinary camera, and a permanent record thus obtained. A very useful and improved type of such an instrument has recently been described by J. B. Johnson.¹ But in other cases, where the

* Presented at the Stated Meeting of The Franklin Institute held Wednesday, April 18, 1923.

¹ *Journ. Opt. Soc. of America*, 6, p. 701 (1922).

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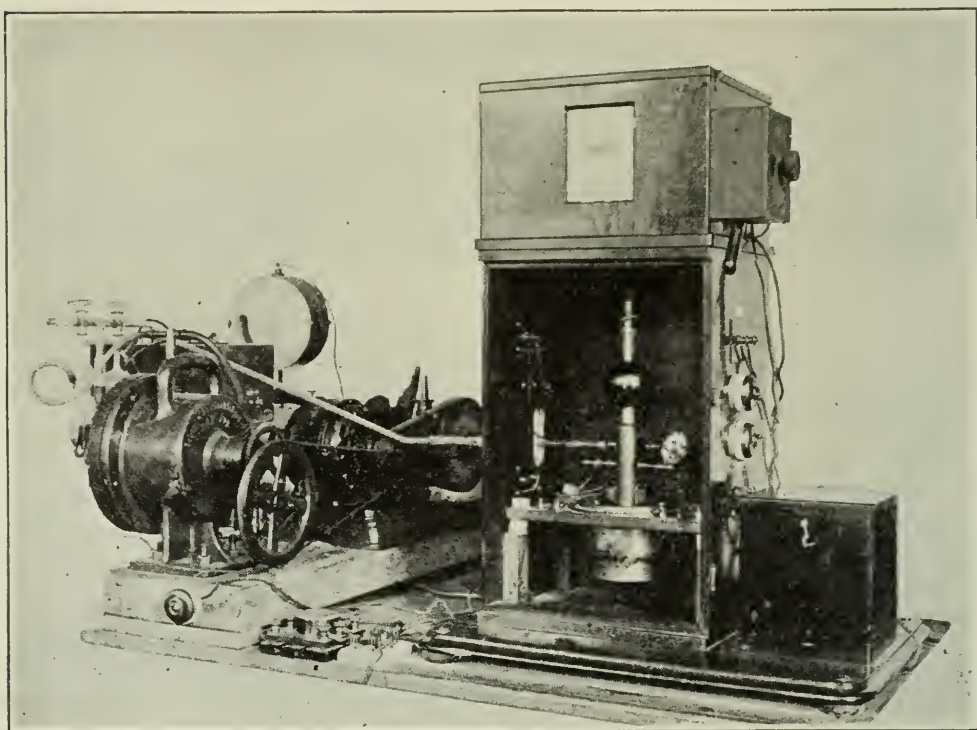
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change is not periodic but impulsive, some other form must be used, as the fluorescent light caused by a single transit of the spot across the screen would fail to leave any impression when photographed as above.

The present paper contains an account of a recent form of oscillograph which was devised by Sir Joseph Thomson and used by the writer. With this instrument impulsive changes in potential

FIG. 1.



Wood's oscillograph.

occurring in less than one ten-thousandth of a second may be measured. By employing the piezo-electric properties of tourmaline, the apparatus has been adapted to measure the time-pressure changes which take place when a gaseous mixture is exploded in a closed vessel similar to the cylinder of an internal combustion engine. The tourmaline crystals transform the pressure variations into alterations in electrical potential.² The same arrangement has been used to investigate the nature of the pressure waves produced in water by the detonation of charges of gun-cotton and T.N.T. under the water. This is the only method

² *Phil. Mag.*, 42, p. 473 (1921).

which will give a continuous and accurate time record of such pressure changes, the recording system possessing practically no inertia. In this type of cathode-ray oscillograph, the photographic plate is placed inside the vacuum tube in front of the fluorescent screen so that the cathode rays impinge directly on the plate and affect it in a single transit. When the plate is removed and developed, a permanent record is obtained. In the Dufour³ oscillograph, the cathode rays also fall directly on a photographic

FIG. 2.

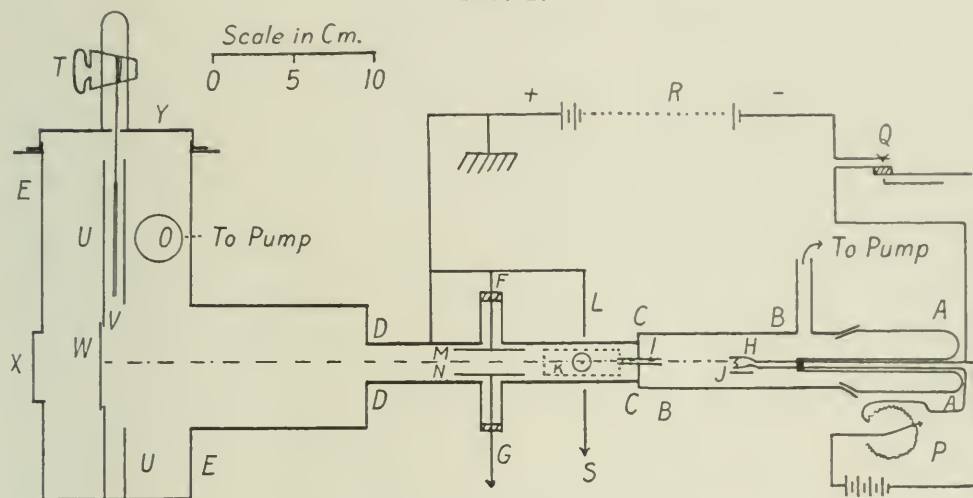


Diagram of oscillograph.

plate, but owing to the larger velocity of the electrons and the method of recording the time intervals, the tube is not very sensitive and is unsuitable for many purposes. Recently A. B. Wood⁴ has described a more robust type of oscillograph (Fig. 1), essentially the same as that previously used by the writer, though differing in some minor details which will be mentioned later.

2. THE OSCILLOGRAPH.

The most recent form of cathode-ray oscillograph used by the writer is shown diagrammatically in Fig. 2, which is drawn to scale. It consists of a ground-glass stopper *AA* which fits into the glass tube *BB*. Two wires are sealed through the stopper as shown and carry at their extremity a small brass cylinder, in the centre of which is a helix *J*, consisting of four or five turns of fine tungsten wire. The other ends of the wire are connected

³ *Journ. de Physique et le Radium*, **1**, p. 147 (1920).

⁴ *Proc. Lond. Phys. Soc.*, **35**, p. 109 (1923).

to an eight-volt storage battery and variable resistance P supported on an insulating stand. By means of this battery and resistance, the tungsten wire J may be heated to any desired temperature. The arrangement is similar to the cathode in an ordinary Coolidge X-ray tube. The glass tube BB is fastened with litharge and glycerine cement to a brass tube CD . This tube is closed at the end CC by a brass plate through the centre of which passes a fine tube I about $\frac{1}{4}$ mm. in diameter. The surface of the plate CC , facing the filament J , is coated with willemite crystals and thus forms a fluorescent screen. Inside the tube CD , and insulated from it, are two sets of parallel plates K and MN , mutually at right angles. These plates are supported by stout brass wires which pass through ebonite plugs, one pair being shown at F and G . The distance apart of the plates M and N may be adjusted by pushing F and G in, or by pulling them out. The two plates shown by the dotted lines at K are also adjustable. The ends of the tubes where the ebonite plugs are inserted are covered with Everett wax, making a vacuum-tight seal. CD is soldered into a wider tube, which in turn is attached to a vertical cylinder EE . This cylinder is fitted with a top Y supporting a glass tube with a stop-cock T , which is ground with a central groove and is used like a windlass.⁵ The top end of this glass tube is sealed. In the centre of the tube EE is a rectangular box UU in which a holder slides, carrying a photographic plate V , the holder being attached by a thread to the cock T , so that it may be raised or lowered by turning the tap. The sensitive side of the photographic plate V faces the tube CD . W is a willemite screen which may be viewed through the glass window X in the side of the cylinder EE as shown. The cover Y fits tightly the top of the cylinder EE and a little wax makes the joint vacuum tight. The whole apparatus is evacuated by means of a "High-vac" vacuum pump to 10^{-3} mm. of mercury pressure, through two tubes, one shown at O and the other attached to B .

One of each pair of deflecting plates ML and K is connected to earth as well as the brass part CDE . R is an Evershed and Vignoles 6000-volt, 15-milliamperes, D. C. generator, the positive terminal of which is earthed and the negative terminal is connected through the key Q with the filament J . When the filament

⁵ See "Rays of Positive Electricity," by Sir Joseph Thomson, 2nd edition, p. 32.

is heated by the battery and the key Q depressed, the strong electrostatic field between J and CC accelerated the electrons emitted by the hot filament towards the plate CC . The cylinder H concentrates the rays along its axis and by observing the willemite screen on CC , one can readily see where the stream is striking. By turning the stopper AA and using an external bar magnet when necessary, part of the beam may be directed through the opening I . The electrons pass between the two pairs of deflecting plates and fall on the screen W , causing a bright green spot. The leads G and S are also temporarily connected to earth while these adjustments are made.

The quality of the spot obtained on the screen W is very important and the successful working of the apparatus depends upon getting this sufficiently bright and small. It was found in the early work with the oscillograph, that the helix in H is the best form of filament and also that the presence of some gas in the tube B as well as the cylinder H helps to concentrate the electrons in a small beam. By judiciously adjusting the temperature of the filament J and the potential of the generator R , it was found that very bright and tiny spots could be obtained on the screen W . The fine spots were much smaller than the optical image of the opening I and produced clear thin lines on the photographic plate, if displaced rapidly across it.

The plate S is attached to the source of potential, the variation of which is to be investigated, such as the insulated pole of a magneto, the exploring electrode in a vacuum tube or the insulated plate of the tourmaline pressure detector to be described later. Any difference in potential between L and S will cause the spot to move in a direction perpendicular to the plane of the paper. The plate G is attached to a Vreeland oscillator, the other terminal of which is connected to earth. This produces a pure sinusoidal alternating e.m.f. between the plates M and N , the period of which may be altered to any desired value by changing the capacity in the usual way.⁶ This alternating electrostatic field between M and N produces a vertical displacement of the spot, which will trace out on the screen W a line which is at right angles to the motion caused by the field between the other pair of plates at K . The Vreeland oscillator thus produces the

⁶ *Phys. Rev.*, 27, p. 286 (1908).

time axis of the oscillograph and since the power consumption is very small, there will be no distortion of the wave form, with the result that the spot will travel up and down with simple harmonic motion. The time taken for it to reach any point in its path from either end is readily obtained when the frequency is known, by the usual simple transformation.

In the earlier type of apparatus used,⁷ a time displacement was produced by a magnetic field produced by an alternating current. This field was parallel to the plates K , but the second pair of plates M and N were not used. Owing to the presence of harmonics in such an alternating current, the vertical motion of the spot was not strictly simple-harmonic, and this fact introduced slight errors in the time scale. Doctor Wood overcomes this difficulty by using the time constant of an electromagnet to give a displacement across his plate. This method has the advantage that the time scale is practically uniform, if proper precautions are taken. If the oscillograph is to be used for impulsive measurements, this method will involve additional mechanical contact arrangements and would be impracticable in cases when the exact time at which the impulsive action takes place cannot be predetermined to within a second.

In the operation of the oscillograph, the screen W is viewed through the window X and all adjustments made until the spot and vertical time line are satisfactory. The key Q is then opened, and the photographic plate V lowered in front of W and thus exposed to the direct action of the electrons. The actual light from the filament which comes through I is not sufficient to affect the plate appreciably. The key Q is so constructed that on depressing it, connection is first made to the generator R , thus producing the cathode-ray beam in the oscillograph. On further depressing the key, a contact is made which results in a change in potential of the plate at K , caused by the phenomenon under investigation. During the interval between the closing of these two circuits, the spot travels several times up and down, producing a vertical zero line on the plate. The horizontal displacement of the spot is proportional to the potential difference between the two plates at K , and so a time-potential curve is obtained on the photographic plate. The key

⁷ Glazebrook, "Dictionary of Applied Physics," 1, p. 76.

Q is now released, air admitted into the apparatus and the plate removed for development. The type of curve obtained will naturally depend upon the nature of the phenomena investigated. To reduce the tracing on the plate to a uniform time scale, the coördinates of points on the curve must be obtained. This is done by placing the plate in a holder similar to that used by Sir Joseph Thomson and the coördinates of the points read.⁸ The time-displacement curve may then be plotted on a uniform scale.

3. APPLICATION OF THE OSCILLOGRAPH TO THE MEASUREMENT OF IMPULSIVE PRESSURES.

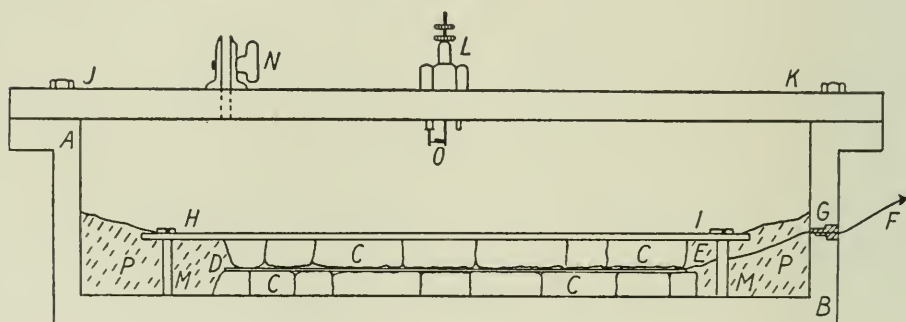
One of the chief applications of this form of oscillograph is to the measurement of very rapid changes in pressure, such as occur in internal combustion engines, or in guns, or in the neighborhood of an explosion under water. In investigating the time-pressure history of such explosions, it is essential for accurate information that the measuring device should have as little inertia as possible. In any crusher gauge or mechanical arrangement there will be errors due to the inertia of the moving system, especially when the changes in pressure are rapid. Moreover, the devices which have been used previously in such investigations will not record large negative changes in pressure—they give $\int P dt$ over short-time intervals and the values of the blocks of momentum vary according to the instrument used. There is a practical limit to the smallness of the time intervals which may be used and so what is usually measured is a series of integrals and not the true pressure-time curve. Sir Joseph Thomson suggested the use of crystals possessing the piezo-electric properties such as tourmaline or quartz, for transforming the pressure waves into corresponding variations in electrical charge. These electrical charges can then be registered on the oscillograph and a true time-pressure curve obtained.

The final type of crystal detector developed for measuring the changes of pressure in gaseous and under water explosions is shown in Fig. 3. It consists of a brass cylinder AB provided with a metal lid JK which may be screwed down with a number of bolts. This box contains two layers of tourmaline crystals CC with a lead plate ED between them. Tourmaline

⁸ "Rays of Positive Electricity," 2nd edition, p. 35.

crystals were used in preference to quartz because the charge produced on the opposite faces of the crystals is directly proportional to the hydrostatic pressure to which the crystals are subjected, whereas in the case of quartz, a lateral pressure produces a charge of opposite sign to that produced by a transverse pressure, a hydrostatic pressure thus producing no appreciable resultant charge. The crystals are mounted in two layers so that all the positive faces of the lower layer are in contact with *DE* and the positive faces of those in the upper layer are downwards, *i.e.*, also in contact with the lead plate. A thin sheet of steel *HI*, fitted with screws *MM*, clamps these crystals down

FIG. 3.



Piezo-crystal detector.

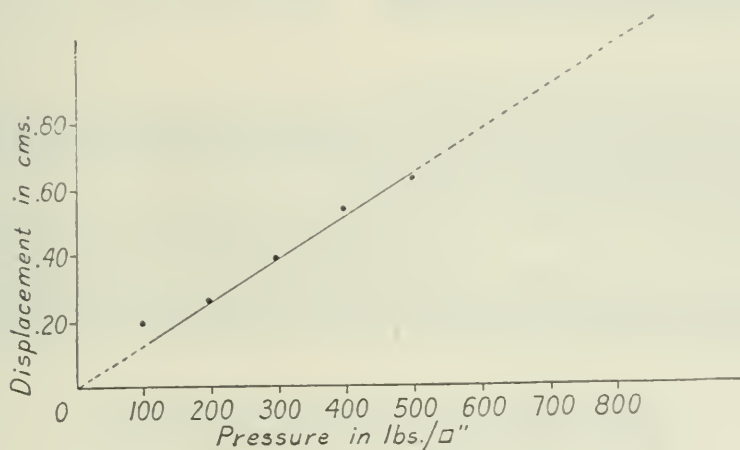
tightly, so that they are held in place and also under pressure against the plate *DE*, which is connected by an insulated wire *F*, passing through the plug *G*, to the insulated plate *S* of the oscillograph. The space *PP* is filled up with vaseline to keep the plate *DE* insulated. The brass cylinder is connected to earth.

Since the crystals are under pressure due to the bolts *MM*, any lessening of the pressure in the region above *HI* will cause a charge on the plate *DE*, which will be of opposite sign to that produced by an increase in pressure on *HI*. Thus it is evident that the arrangement will register negative as well as positive pressures. This is an important advantage which this device has over previous types of gauges. Moreover, since the pressure wave has only to pass to the crystal in order to produce the electrical separation, *i.e.*, the charge on the plate *DE*, no bodily motion of the crystals or any other part of the apparatus is necessary.

To use this detector for studying the time-pressure changes

in explosions, the vessel must be calibrated. This is done by placing the vessel in the position in which it is to be used in the investigation and connecting the wire *F* to the oscillograph. The lid *JK* is bolted down and the pot is completely filled with gasolene or some other liquid which is not a very good electrical conductor. A static pressure is applied to the liquid in the vessel by means of an oil pump attached to the tap *N*. The resulting pressure in the vessel produces a corresponding charge on the plate *DE*. This charge raises the potential of the plate of the oscillograph and the cathode beam is accordingly deflected. The amount of this deflection is found to be directly propor-

FIG. 4.

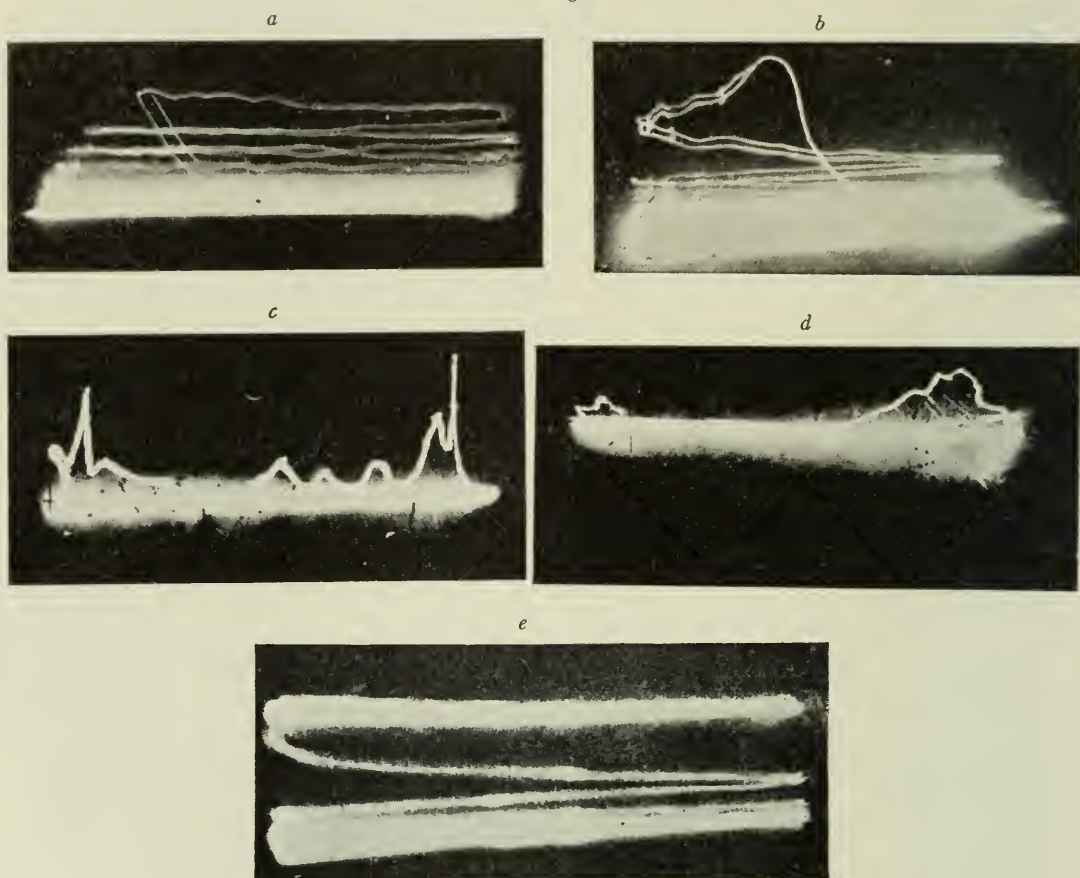


Calibration curve of piezo-crystal detector.

tional to the pressure applied to the crystals. The pressures are read from a gauge attached to the pump and the deflections measured on the photographic plate of the oscillograph. The vessel is thus calibrated *in situ* and therefore no corrections are necessary for capacity as this is not altered during an investigation. If a pressure is applied to the crystal detector and the wire *F* momentarily earthed so as to remove the charge caused by the increase in pressure, then on releasing this pressure, there will be a deflection of the cathode-ray beam in a direction opposite to that caused when a pressure is applied. The charge produced on the release of the pressure equals that caused by the application of the pressure, but is of opposite sign. Since a pressure may be released more rapidly than applied, the vessels were usually calibrated by releasing the pressures. A typical calibration curve obtained in this way is shown in Fig. 4.

The calibrated vessel may now be used to investigate the time-pressure history of gaseous explosions. When used for such purposes, an ordinary automobile spark plug *L* is fitted into the lid (Fig. 3) and the sparking points are joined by a thin wire *O*. This wire is connected with a battery through the

FIG. 5.



Examples of photographic records obtained.

- (a) and (b) Explosion of mixture of electrolytic gas and air.
- (c) Explosion of guncotton under water showing echo also.
- (d) Explosion of T.N.T. under water, showing echo also.
- (e) Time of adjustment of potential in a Geissler tube.

N. B. Plates *a* to *d* had to be touched up in places with Chinese white for reproduction purposes, but *e* is untouched.

second contact of the key *Q* (Fig. 2). The vessel is exhausted through the tap *N* and the explosive mixture introduced. The oscillograph is then adjusted, the photographic plate lowered into position and the key *Q* depressed. Before the gas is detonated the cathode-ray beam will execute several vertical oscillations in its zero position and a zero line is thus traced

on the plate. When the explosion takes place, by the heating of the wire *O*, the beam will be deflected horizontally, and the combination of the two motions gives the time-pressure record. Fig. 5 is a reproduction of some curves obtained in photographic plates in this way. It frequently happens that there are two tracing spots very close together and in such cases each spot traces out its own path. Either of these paths may be measured up for plotting the time-pressure curve on a uniform time scale. In

FIG. 6.

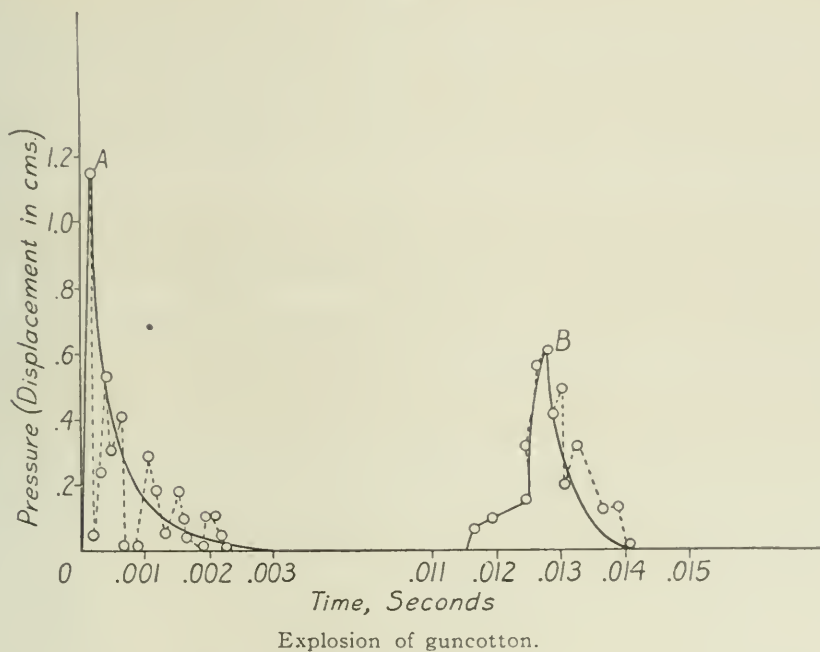


Fig. 6 are given the time-pressure curves for three different mixtures of electrolytic gas and air, obtained with this apparatus. It is apparent from these results that the scheme has an important application in the study of the detonation of various mixtures of oils and vapors for use in internal combustion engines. Moreover, by placing crystals in the piston of a gasolene engine, or in any desired part of the walls, the internal ballistics of the engine may be studied. With the continual growth in the use of internal combustion engines, it is necessary that they should be operated with the greatest economy. The piezo-electric method described above places an instrument in the hands of an engineer with which he may determine the most efficient and economical explosive mixtures for use in such engines.

The application of the piezo-electric method of measuring explosion pressures in guns is at once apparent. J. C. Karcher⁹ has recently used the piezo-electric properties of quartz in conjunction with a ballistic *galvanometer* for such a purpose. The use of the galvanometer has the disadvantage that in cases where the initial and final pressures are the same, and the pressure changes take place very rapidly, the resulting charge passing through the galvanometer is zero and no deflection will result. By substituting the cathode-ray oscillograph for the galvanometer, the method would be practical in all cases.

The apparatus may also be used for the determination of the specific heats of gases at high temperatures by the usual constant volume method.¹⁰ The outstanding advantage of this device, over all previous methods, is, that the apparatus has practically no inertia.

By removing the lid *JK* (Fig. 3) and placing the crystal detector under water, the arrangement has been used for measuring the pressure waves resulting from the explosion of small mines in water near the vessel. Fig. 6 represents a typical time record of the pressure wave at 12 feet from a 2¼-pound charge of dry guncotton detonated under water. In the figure, *A* represents the direct wave and *B* is the echo reflected from the bottom. By having two such detector vessels placed in the water at a fixed distance apart and arranging the crystals in one so as to give a positive charge to the deflecting plate of the oscillograph, while the other produces a negative charge on the same deflecting plate, due to the pressure wave, the velocity of propagation of the wave has been determined. The average of a number of observations, taken in this manner, gave a velocity of approximately 5100 feet a second, a value slightly in excess of the velocity of sound. Such experiments will also show the change in the form of the wave with distance from the source.

The experiments described above will give a general idea of the wide and varied application which this method offers for the measurement of impulsive pressures. By inserting suitably mounted crystals of quartz or tourmaline in the struts and frame rods of aeroplanes, the rapid variations in both tensions and compressions in these members may be investigated when the aero-

⁹ Bureau of Standards, Scient. Papers, 18, p. 257 (1922).

¹⁰ M. Pier, *Zeitschr. f. Elektrochemie*, 16, p. 897 (1910).

plane is in actual flight. This would necessitate an alteration in the cathode-ray tube so that it would be more compact, but that could be accomplished by suitable design.

4. THE MEASUREMENT OF RAPID CHANGES IN ELECTRICAL POTENTIAL.

Besides the use of the Thomson cathode-ray oscillograph for the measurement of pressures, the instrument has an important application to the investigation of electrical oscillations, both periodic and impulsive. Wood's paper, which has already been referred to, gives some results obtained with the oscillograph in measuring high-frequency oscillations. The instrument may also be used to measure the nature of the electrical surges on transmission wires, the characteristics of the magneto discharge, the nature of lightning flashes and many other phenomena of an impulsive nature of short duration. As illustrations of the application of the oscillograph in this connection, two investigations performed by the writer will be briefly mentioned.

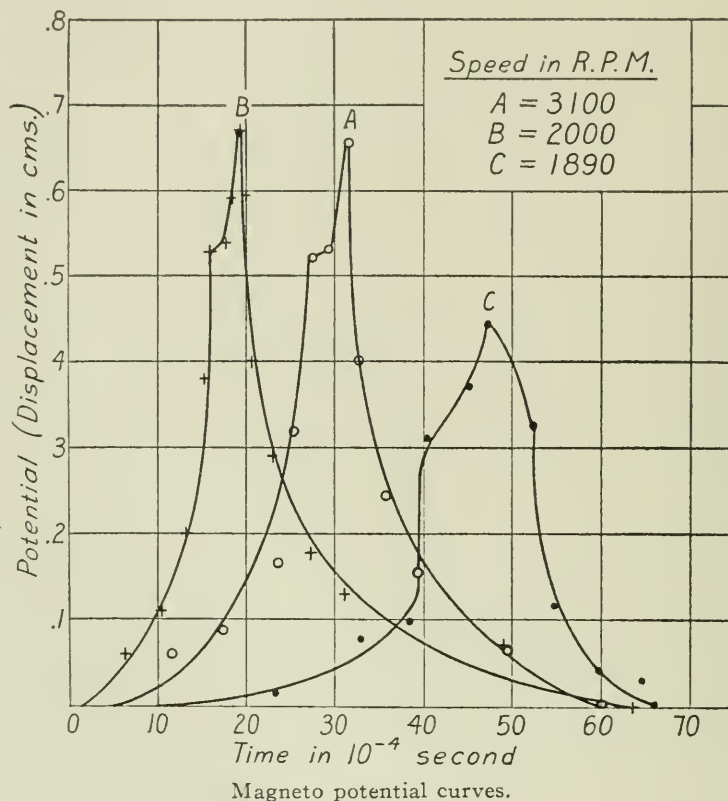
The experimental investigation of the theory of the high-tension magneto is a matter of great importance to the automobile manufacturer. It is well known that some types of magnetos are much more efficient and reliable than others and the reason for this is not always apparent. Prof. Taylor Jones¹¹ has given a theory of the magneto and Dr. N. Campbell¹² has described some experiments investigating the characteristics of such magnetos. The method adopted by Campbell for measuring the time-potential curves in the magneto was ingenious, but a separate adjustment and experiment was necessary for determining each point on his curve. The *continuous* time-potential curve may, however, be easily obtained in a single exposure with the oscillograph. To do this, the plates *L* and *S* of the oscillograph (Fig. 2) are connected in parallel across the spark gap of the magneto. The magneto was driven by a motor, and while it was running discharges occurred between the usual points of the spark plug. The insulated pole of the plug was connected to the plate *S* of the oscillograph. The difference of potential between the plates *S* and *L* will vary with the potential difference between the points of the spark plug. By depressing the key *Q* for an instant, the cathode rays pass from the filament and a time

¹¹ *Phil. Mag.*, [6], 36, p. 145 (1918).

¹² *Phil. Mag.*, [6], 37, pp. 284, 372 (1919).

record is obtained on the photographic plate of the potential variations. In some cases two sparks occurred while the key Q was depressed and two curves were found upon the plate. Both tracings were found to give identical curves within the limit of error of the oscillograph. In Fig. 7 are given the time-potential curves for three different speeds of the magneto. The results

FIG. 7.



are in general agreement with those found by Doctor Campbell. In this way, the effect of changing the windings, shape and construction of the various parts of a magneto may be investigated with the object of obtaining the optimum arrangement for maximum efficiency.

Another interesting investigation, which this oscillograph made possible, is the determination of the time required for the initial discharge in a Geissler tube to reach its equilibrium state. The investigation was suggested to the writer by Sir Joseph Thomson and the results showed that the time required to establish the final distribution of potential along the tube depended

upon the nature of the gas in the tube.¹³ An insulated electrode, which could be moved in the vacuum tube to any point between the main two electrodes, was connected to the insulated plate of the oscillograph, the cathode of the discharge tube being connected to earth. As the potential rose in the neighborhood of the exploring electrode, the beam was deflected and the time required for equilibrium to be established was thus determined. Changes in potential of a few volts which took place in a one hundred-thousandth of a second were measured with this device. In the case of air, the times required for the discharge to reach a steady condition varied from 1 to 80 ten-thousandths of a second.

5. CONCLUSION.

The type of cathode-ray oscillograph described in this paper supplies an instrument which has long been wanted in many investigations. In its robust form it will be useful to the engineer for the measurement of very rapid potential or pressure changes of an impulsive nature. The few experiments described above will, in a general way, indicate some of the various applications and possibilities of the method. This oscillograph has made it possible to measure changes in pressure or potential which occur in a hundred-thousandth of a second or less. New avenues of research are consequently opened for investigation which should result in practical results of great economic and commercial value.

The writer wishes to acknowledge his indebtedness to Sir Joseph Thomson for entrusting to him the development of this apparatus and also for his continual advice and encouragement during the investigations described. He also wishes to thank Dr. A. S. Eve for his helpful suggestions in the writing of this paper.

Lightning and Fires. (Clip Sheet, U. S. Department of Agriculture, No. 276.)—The annual destruction due to lightning fires in the United States is estimated to be as much as \$20,000,000. In one State alone, Iowa, during the four years ending with 1922, the loss as given by the State fire marshal was \$1,363,704, of which 61 per cent. was due to fires in farm barns. Very nearly all of such loss is preventable by proper rodding, says the Weather Bureau of the United States Department of Agriculture, in commenting on this tremendous loss.

¹³ Thesis submitted for Ph.D. degree at Cambridge University, 1922.

Some Observations on Alpha Particle Tracks in a Magnetic Field. P. KAPITZKA. (*Proc. Cam. Phil. Soc.*, Lent Term, 1923.)—When an alpha particle passes through a gas, it breaks up some of the atoms in its path. C. T. R. Wilson decades ago showed how to make the path of the particle visible by rapidly expanding the gas and thus letting the atomic fragments serve as nuclei for the condensation of the water vapor present. This method has provided much information on the nature of the collisions of the particle with the atoms in its way. "In the recent experiments of Blackett, it was shown that by studying the forks and the kinks which occasionally occur on the alpha tracks, it is possible to obtain the velocity of an alpha particle at any point on the path." But how shall the velocity be found in the absence of forks and kinks? The answer is found in the application of a magnetic field. This changes the paths of the particles from straight lines to curved lines, and from the radius of curvature at a point can be calculated the ratio of the velocity of the particle at that point to the electric charge at that position upon it. To bend the path sufficiently a strong magnetic field is essential, and this requires a strong current. Since, however, the particle traverses with a velocity that is an appreciable fraction of the velocity of light the few centimetres in the length of its path, it is not necessary that this large current should flow longer than for a small part of a second. By using a special accumulator 8000 amperes were furnished to the coil of an electromagnet for .002 second. The brevity of the duration kept the current from fusing the coils. "In these experiments the field which was produced in a bobbin surrounding a circular Wilson chamber of 2.2 cm. in diameter, reached 75,000 gauss. . . . A special shutter which let the alpha particles into the expansion chamber only during 0.001 second is timed with the current in the coil." Photographs of the cloud tracks thus curved show that each track has a curvature of its own. The cause of this difference awaits an explanation. "About 8 mm. from the end of the range all behave in a similar way and have nearly the same average charge + 1.5e." This diversity in curvature may be discouraging to him who first noted it, but so much has already been learned from the kinks and bends of the tracks that one may well hope to gain fresh knowledge of the mechanism of collision from the interpretation of the tracks described in the magnetic field.

G. F. S.

Hexanitrite Test for Lead. LAWRENCE T. FAIRHALL, of Harvard University (*Jour. Biol. Chem.*, 1923, 57, 455-461), has studied the hexanitrite microchemical test for lead. This test depends on the crystallization of regular rectangular plates or cubes of the hexanitrite of potassium, copper and lead of the formula $K_2CuPb(NO_2)_6$ from an aqueous solution. The test will reveal the presence of as small an amount as 0.001 milligram of lead in 15 c.c. of a solution containing a considerable amount of other inorganic salts.

J. S. H.

THE MAIN PIERS OF THE BRIDGE OVER THE DELAWARE RIVER, BETWEEN PHILADELPHIA AND CAMDEN.*

I. DESIGN.

BY

CLEMENT E. CHASE, C.E.

Principal Assistant Engineer, Delaware River Bridge Joint Commission.

AS THE first step in translating into actuality the century-old project for a bridge over the Delaware River between Philadelphia and Camden, the building of the two river piers has commanded special attention.

The completed piers are notable examples of massive granite masonry, conspicuous in a day when granite masonry has been largely displaced by hastier and cheaper all-concrete construction. The ashlar courses have a rise of from three feet five and one-half inches to two feet six inches, and individual stones weigh as much as nineteen tons. The lower half of the shaft exposed above water level is "rock-" or "quarry-face" ashlar; the upper half smooth finished—what the quarry man terms "four-cut." The proportioning of the mass was most carefully studied in relation to the design of the steel shaft of the tower that was to surmount it. As in all other parts of this structure, the attempt has been made to adopt that design which, within the limits of good engineering, would have the greatest architectural merit. The full measure of success with which that effort has met can only properly be judged when the bridge as a whole shall have been completed.

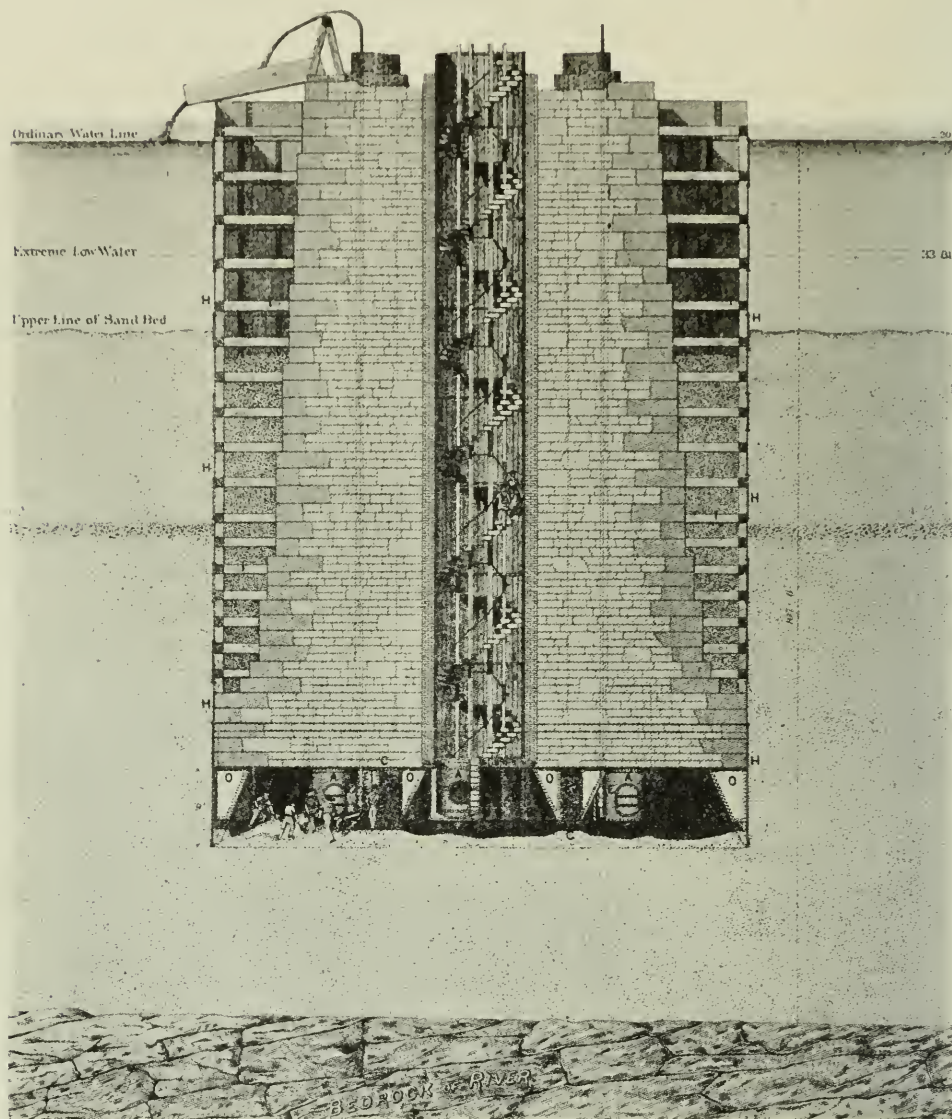
From the engineer's point of view, the principal interest in the two piers attaches to the means used in their construction—the design of the caissons and their handling during sinking. Passing attention, however, can be given to the conditions which governed the location and dimensions of the piers.

The Delaware, as a navigable stream, comes under the jurisdiction of the War Department. The terms of the permit signed by the Secretary of War required the bridge to span without piers

* Presented at the Stated Meeting of The Franklin Institute held Wednesday, February 21, 1923.

between the pierhead lines on the two sides of the river. At the selected location on the line from Franklin Square in Philadelphia to Pearl Street in Camden, this requirement fixed the span at

FIG. 1.



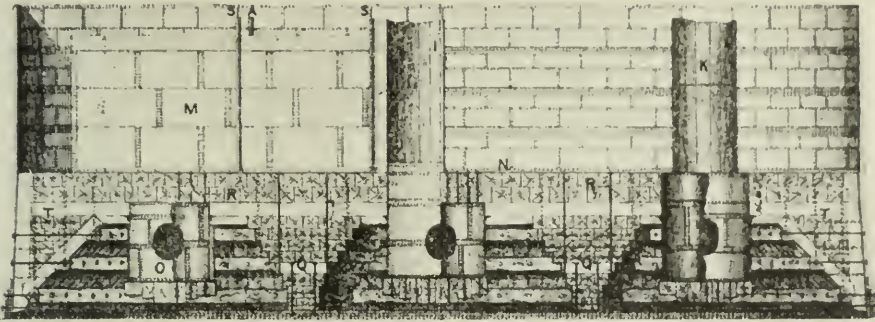
Caisson—east pier—Eads Bridge.

1750 feet, centre to centre of piers. Preliminary borings at this site had shown bed rock of good quality to be readily accessible by the ordinary methods of pneumatic caisson foundation. The length of the pier was determined by the necessary distance apart of the two main cables of the bridge and by considerations of procuring a proper width of masonry outside of the tower

bearings. The width of the pier had to be great enough to secure complete stability and prevent excessive bearing pressures at the edge from wind load and unbalanced cable pull. Each foot of additional width cost not only directly in masonry, but also indirectly in the increased span length involved.

During the design of the foundations and preliminary to the letting of the construction contracts, unusually thorough test borings were put down by churn and diamond drill methods over the entire area of each pier. These gave advance warning of irregularities in the level of the rock surface, knowledge as to

FIG. 2.



Caisson—east abutment—Eads Bridge.

the quality of the rock that would be encountered, and assurance that it was not underlaid with soft strata. Some of the holes penetrated thirty feet into the mica schist rock.

Bed rock on the Philadelphia side of the river was found to be from about 60 feet to 78 feet below mean high water and on the New Jersey side about 24 feet deeper. The complete information secured was of great assistance to bidders and to the successful contractors, in their handling of the work.

Alternate studies were made of foundations employing one large caisson or two smaller ones. In the latter case the difficulties and expense of securing a proper tying together of the pier shaft ruled out the scheme. With foundation by a single caisson for each pier decided upon, it was very apparent that the problem of adequate caisson design was a most important one. In Table I are given the sizes of a number of the largest pneumatic caissons that have been constructed for bridge foundations, showing those of the Delaware River Bridge to be fourth in size of those listed.

It may surprise some to note how much larger the Brooklyn Bridge caisson was than any built in the fifty years since.

TABLE I.

Date.	Bridge.	Dimensions.		Area in sq. ft.
1871	N. Y. pier, Brooklyn Bridge	102	× 172	17,544
1898	Alexander III Bridge, Paris	110	× 145	15,850
1901	Manhattan Bridge, New York	78	× 144	11,232
1922	Delaware River Bridge	70	× 143	10,010
1910	Quebec	55	× 180	9,900
1914	Metropolis	60½	× 110½	6,655
1869	East Abutment, Eads Bridge	72½	× 82 (hex)	6,000

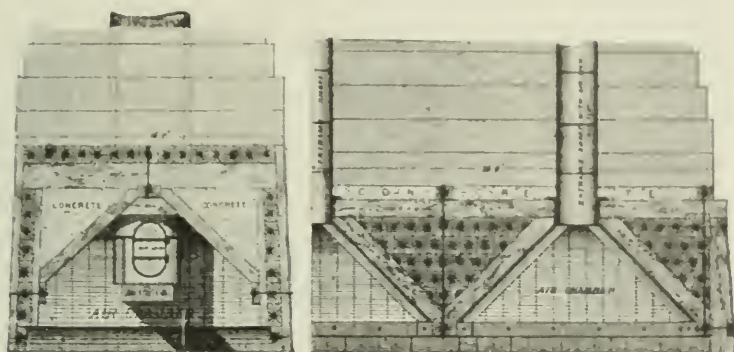
In those fifty years, however, great changes have occurred in pneumatic foundation practice. Much that was of the nature of a novel expedient in Brooklyn Bridge construction days has since become mere routine. Prof. Ira O. Baker tells of the interest aroused in Chicago at the time blasting was first proposed to be done under air in the Brooklyn caissons. The Chicago papers carried daily bulletins as to the success of the operation. To-day blasting under air is resorted to with as little ado as pick and shovel work. The ingenious but elaborate sand pump, developed by Eads, has been simplified until all is eliminated but the flexible hose, through which the mixture of sand and water, or air and water, is expelled from the bottom of the working chamber. Candles were at first the only source of illumination in the working chamber. These burned rapidly, with excessive smoke that blackened the lungs of the workmen. The open flames made the danger of fire a constant menace. Electric illumination has changed all this, and vastly improved working conditions. One is struck, however, with the fact that these improvements have been far more striking in technique and equipment than in the design of the caissons themselves.

Caisson design has much in common with that of ships; the forces are large and, to an even greater extent than in naval architecture, indeterminate. Construction has been governed largely by rule of thumb, and experience and precedent more relied upon than any analysis of the forces involved. Progress under these conditions is naturally a matter of slow development and improvement.

It would probably give a better perspective to a view of the development of caisson design to retrace briefly the history of pneumatic foundations.

The first suggestion of the process is to be found in the invention in 1717 by Doctor Halley, Secretary of the Royal Society of London, of a method for furnishing a continuous air supply to a diving bell. The idea, however, except for its use by Smeaton at Hexham Bridge, lay practically dormant for more than a hundred years until the great burst of engineering activity in England in the early nineteenth century served to turn men's minds to the

FIG. 3.

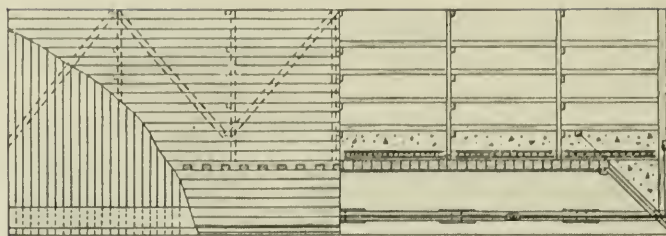


Caissons—east approach piers—Eads Bridge.

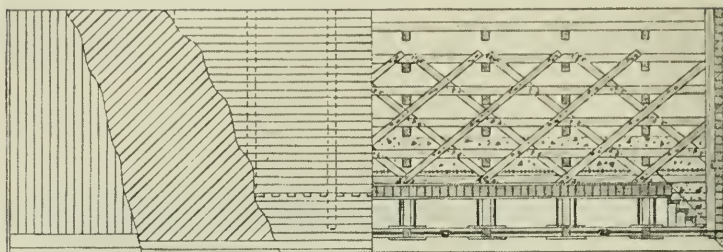
need for means of carrying on work under water, for the construction of tunnels, marine structures and bridge piers. In 1830 Thomas Cochrane, an adventurous Scotch nobleman and soldier of fortune, applied for a patent in which he fully set forth the essentials of caisson and air-lock as we now know them. His device was suggested by the difficulties which were then being encountered by the elder Brunel in the attempt to construct the first tunnel under the Thames.¹ In Woodward's history of the Eads Bridge, it is stated that Triger, a French engineer, made the first actual use of compressed air methods. This was in connection with the sinking of a mine shaft in the year 1841. Based on that experience, he later suggested the use of the same method for bridge foundations. Such a use was made of the new method at Rochester, England, in 1851, and in the United States in 1852, in the foundations of bridges over the Peedee and Santee Rivers. The foundations for these last were cast-iron cylinders.

¹From memorandum by Daniel E. Moran.

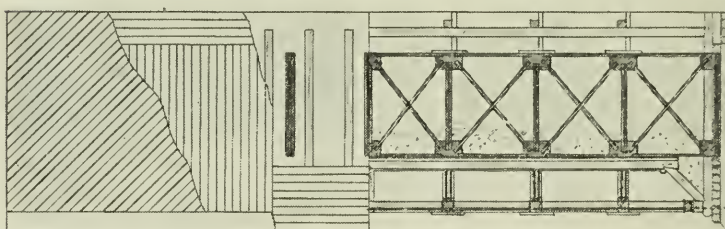
FIG. 4.



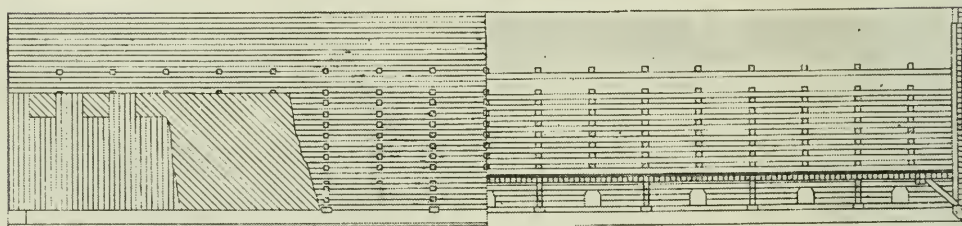
McKinley Bridge, St. Louis, Mo. Length 70' 0".



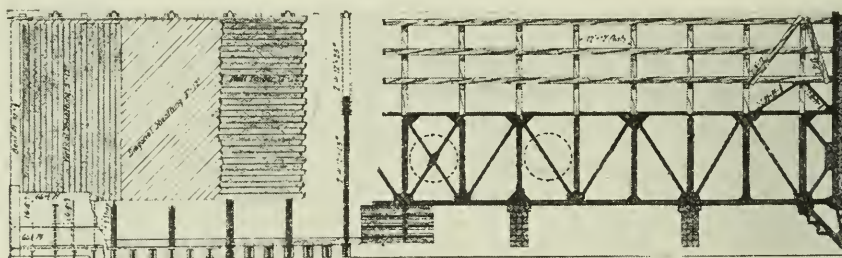
Municipal Bridge, St. Louis, Mo. Length 90' 3".



Metropolis Bridge. Length 110' 6".



Quebec Bridge. Length 180' 0".



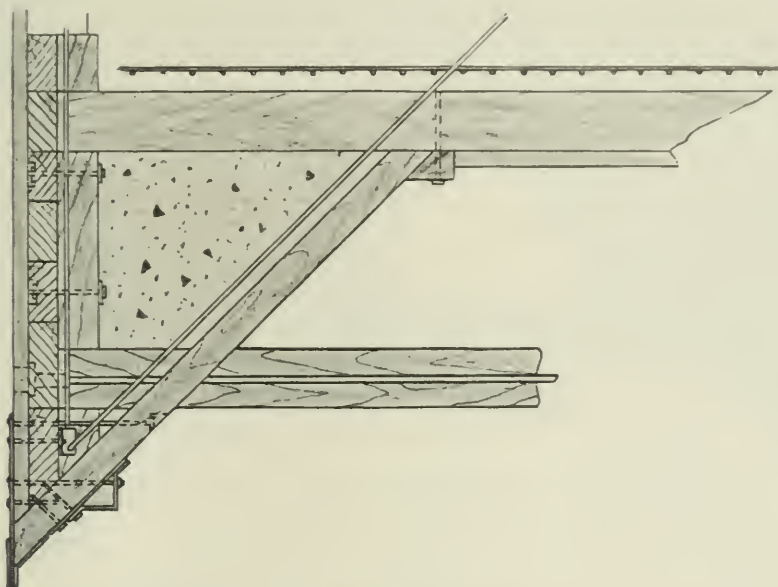
Delaware River Bridge. Length 143' 0".

Elevations and sections of caissons.

called "pneumatic piles." In 1854 Brunel used the scheme on a larger scale on his Saltash Bridge, and in 1859 it was used by St. Denis for the Rhine Bridge at Kehl. From that time on, the method grew in favor and was widely adopted in Europe.

In 1868, Captain Eads, in the first plans for his bridge over the Mississippi, proposed to found the main piers within open wells, sunk to bed rock by open dredging. On his trip to Europe, however, in 1869, he saw the river piers which were then being built at Vichy and talked with the resident engineer, M. Audernt, who had been building foundations by the pneumatic process for fourteen years, during which time he had put down forty bridge piers.

FIG. 5a.



McKinley Bridge, St. Louis, Mo. Caisson wall and cutting edge.

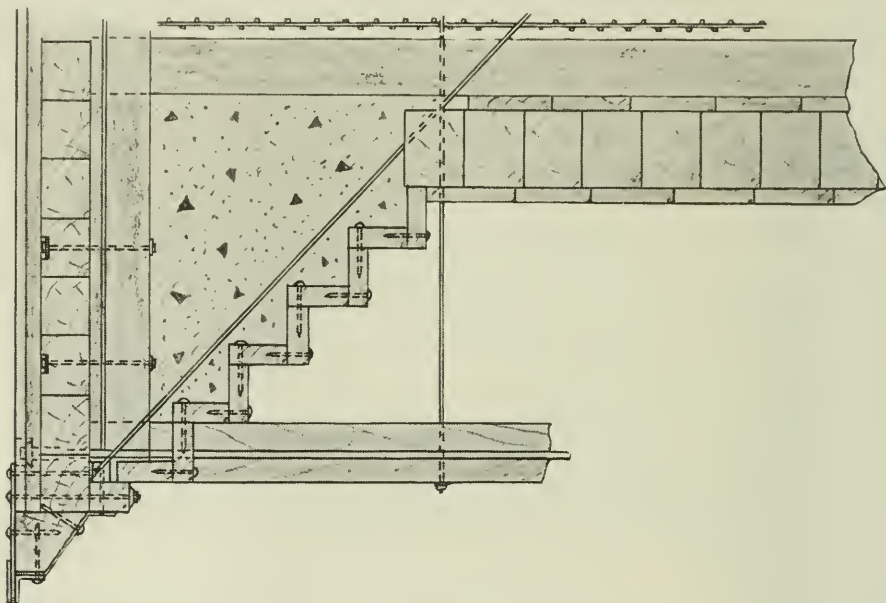
Eads also consulted with British engineers who had used the process and on his return to St. Louis in April, 1869, decided to use compressed air on the two river piers, though the depths to which these caissons must be sunk were greater than any hitherto attempted. No time was lost in carrying the plan to execution, for on October 17th of that year the caisson of the east pier was launched and between that date and April, 1871, the west pier and the east abutment caisson were also constructed by the same method.

These pioneers soon discovered for themselves many novel effects of work in compressed air. Woodward remarks that they found that one could not whistle and that candles burned very

rapidly, creating a great deal of soot. Some of the workmen shortly developed the ailment peculiar to work under compressed air and we can detect the origin of its common name, the "bends," in Woodward's narrative:

"A workman walking about with difficult step and a slight stoop was at first regarded as a fit object for jokes, and cases of paralysis and cramp soon became popularly known by the name of 'Grecian bend' "²—then the mode of fashionable ladies." The

FIG. 5b.



Municipal Bridge, St. Louis, Mo. Caisson wall and cutting edge.

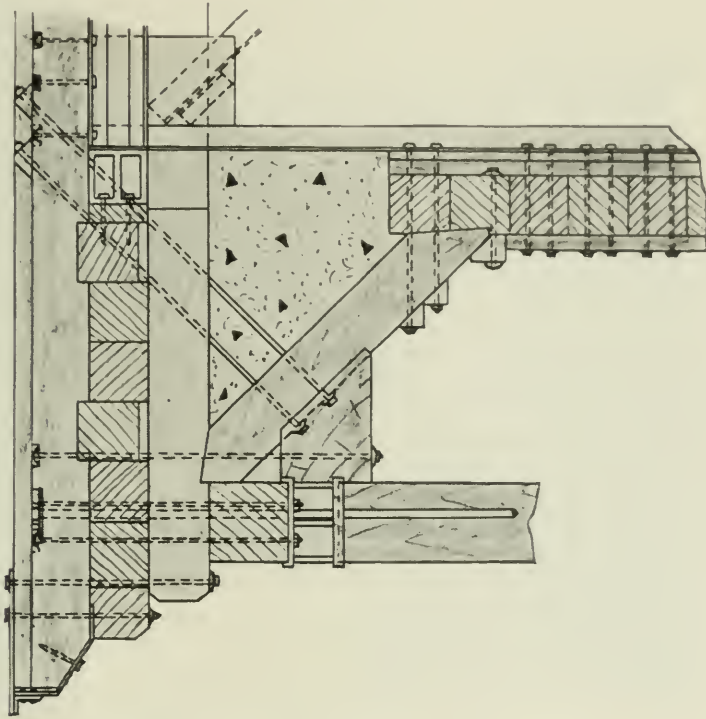
bends were, as they soon learned, no laughing matter, however, at that time, for in the sinking of the east abutment eleven men lost their lives from this cause. The "caisson disease" has been given much study since that time and the precautions by which its seriousness can be minimized have been well established. Special consideration was given to these in the drafting of the specifications for the Delaware River Bridge work.

At the same time that the work was going on in St. Louis, the foundations of the Brooklyn Bridge were being constructed in New York by the same process. The caisson for the Brooklyn pier was launched in March of 1870 and the New York caisson, which still holds the record of being the largest ever built, was launched in May of the following year.

² Woodward, p. 247.

The first caisson designed by Captain Eads followed the precedent of European practice in being largely constructed of metal. Wrought iron, at that time, cost from 6 to 7 cents a pound in this country. The same economic conditions which led later to the development of the typical American type of timber caisson, influenced the St. Louis Bridge work so that, by the time the third caisson was constructed, Eads had adopted timber roof

FIG. 5c.



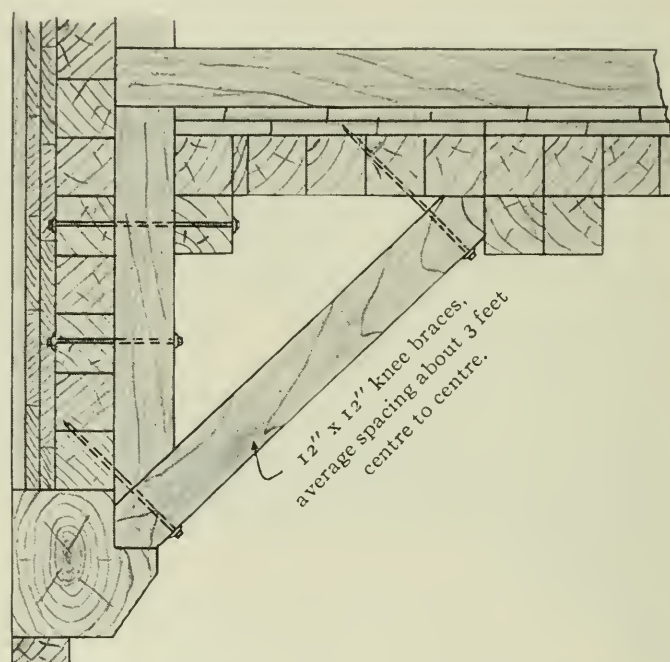
Metropolis Bridge. Caisson wall and cutting edge.

and side walls, though retaining a metal crib above the working chamber. Under American conditions it was quicker and cheaper to build caisson structures in timber than to secure the equivalent strength in metal. In their prodigal use of timber the Brooklyn Bridge caissons set another record which has held ever since. The caisson for the New York pier had twenty-two feet of solid 12×12 timbers over the working chamber for a caisson 102×172 feet in plan. Later American engineers tended to follow the lines of this precedent. William Patton, in the caissons for the B. and O. Railroad Bridge at Havre de Grace, used eight feet of solid timber above the working chamber for a caisson

only 31×79 feet in plan. The modifications in caisson design which have come since that time have been the result of changing economic conditions in this country and the growing development of other types of construction, such as reinforced concrete and structural steel.

In the development of the design for the Delaware River Bridge caissons, twelve distinct studies were made. The first of these was for all-timber construction, along conventional lines.

FIG. 5*d*.



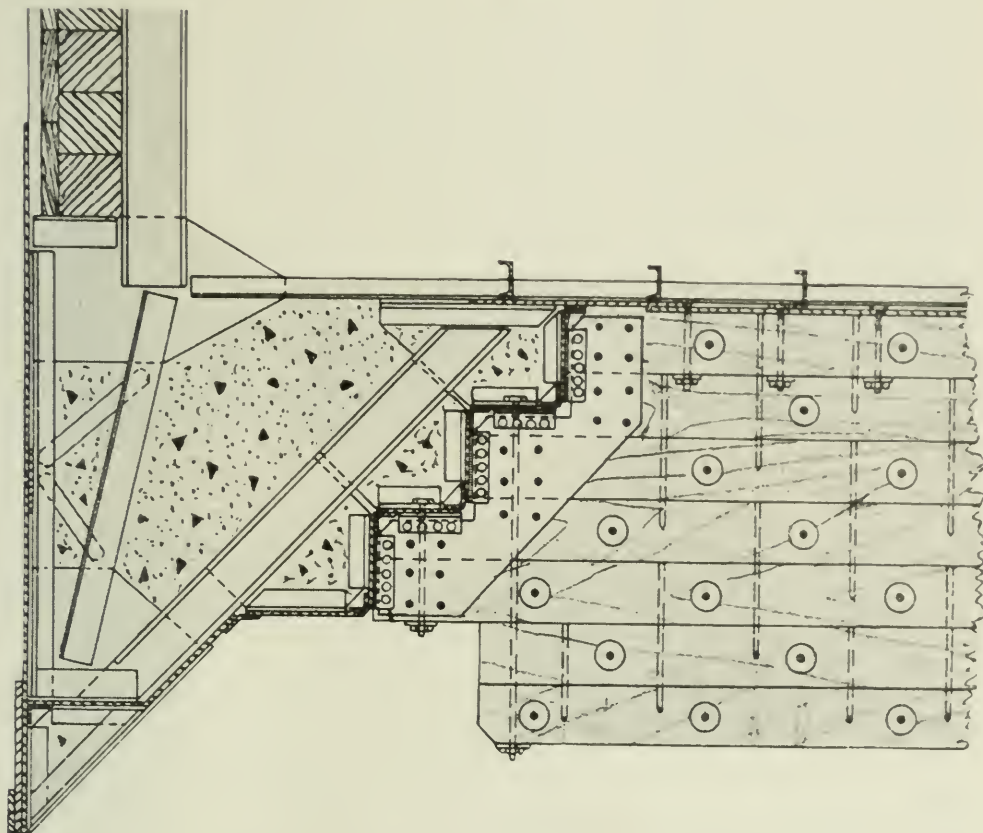
Quebec Bridge. Caisson wall and cutting edge.

The last, and adopted, design used steel for all parts except walls above the working chamber, the upper bracing and the cofferdams. So successful were these caissons in practice that the only regret of the designers has been that even the side walls and bracing were not also of steel. The design in its evolution followed a close parallel to the historical development of this type of structure.

To provide strength against longitudinal and transverse bending forces, the earlier caissons relied on their massive solid timber roofs and, later, on intersecting crib work built up above the roof. The caissons of the second Quebec Bridge were typical of this type of construction. The troubles which developed with the 180-foot

Quebec Bridge caisson during sinking would tend to show that in it, reliance on crib work for bracing had been carried to an extreme. This caisson, through a failure of its pumps, grounded prematurely on a bottom which had not yet been properly prepared, causing a sag at the centre of fifteen inches, later increasing to two and one-half feet. Eight feet of concrete, which had been

FIG. 5c.

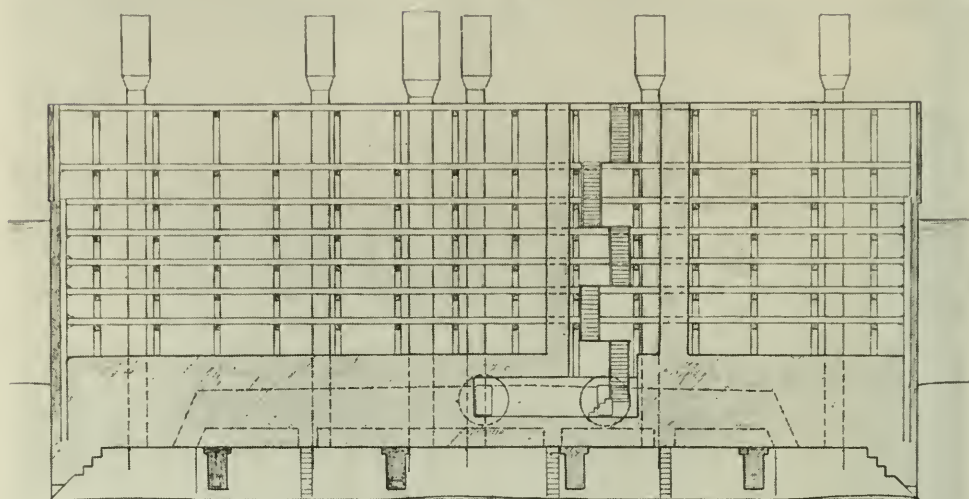


Delaware River Bridge. Caisson wall and cutting edge.

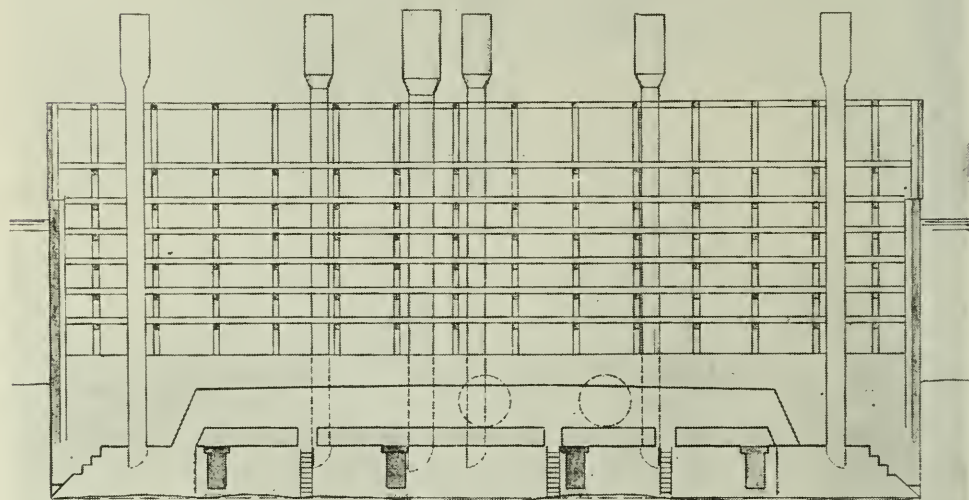
placed over the roof and in the interstices between the cribbing, had to be removed before the caisson could be refloated and taken back to dry-dock for repairs. It was found, on examination, that the caisson had landed on a boulder at one corner, setting up stresses which in all probability could not have been resisted by any caisson design developed up to that time.

Within the last fifteen or twenty years, the development of reinforced concrete has made its influence felt in caisson construction. All-concrete ones have been built, some of them quite successful in operation. Studies of this type were included

among those made for the Delaware River Bridge, but did not compare favorably with the other designs. A more limited use of reinforced concrete in combination with timber has been found



Caisson A—section through stairwell.



Caisson A—section through emergency chamber.

economical. In this type, quite largely developed by the Missouri Valley Bridge and Iron Company in the Middle West, reliance is placed in a reinforced concrete slab for the strength of working

chamber roof and side walls. In this way the thickness and amount of timber used has been materially reduced until it serves as hardly more than a substantial form, capable of standing launching stresses and resisting hydraulic pressure on the side walls above the concrete level. To secure greater rigidity of the timber construction at launching, diagonal braces were spiked and bolted to the longitudinal bracing of the St. Louis Municipal Bridge caissons. In the caissons for the Metropolis Bridge over the Ohio River, steel trusses were utilized above the roof of the working chamber. These proved very successful.

The first designs of the Delaware River Bridge made use of close timber cribbing of the Quebec type for interior bracing and stiffening. Later, combination trusses, with steel tension rods, cast-iron blocks and timber chords and posts were studied. On analysis of the design finally developed for this type of truss it was found that there was enough metal in each of them to make a good steel truss. With the favorable recommendation of the engineers who had sunk the Metropolis caissons, steel trusses were adopted as soon as satisfactory details had been developed. Main reliance for stiffening the roof was placed in the transverse trusses, the longitudinal system being considered merely as distributing girders. The main longitudinal strength of the caisson lay in the side walls, with their double layer of sheathing.

With steel trusses decided upon, the use of a steel roof for the working chamber followed naturally, as it cost about one dollar less per square foot of roof and entirely eliminated the fire danger, which is always present in the timber roof.

With steel adopted for working chamber roof and the trusses above, the next step was the development of a steel working chamber wall or "toe," filled and stiffened with concrete after launching. Above the working chamber the timber walls of the earlier designs were retained.

Retracing the historical development of this element of the caisson, we find that Eads in his first St. Louis Bridge pier used a metal cutting edge, an iron shell braced by riveted iron brackets. In the succeeding piers of that bridge V-shaped walls were used, either of solid timber or of timber, concrete filled. In the later extensive use of the pneumatic caisson by American engineers both the V-shaped walls and parallel side walls of timber were utilized. G. S. Morison used 17×17 inch timbers for the

inside sloping wall of his Bellfontaine Bridge caissons in 1892. The parallel-sided timber walls, however, were even more commonly used despite the fact that partial failures of this type of wall have quite frequently occurred during sinking. In the light timber and concrete caissons previously referred to, the Missouri Valley Bridge and Iron Company adopted the V-shaped toe filled with concrete and reinforced with steel rods. Their St. Louis Municipal Bridge caissons had a stepped inner wall because of the engineer's objection to a possible cleavage plane which might be produced in the finished pier by an inclined surface. All these types of caisson wall have depended very largely upon interior bracing across the working chamber for their strength, especially so in the case of the parallel-sided timber walls. Recent examples were the Metropolis and Quebec caissons, and in both cases there was evidence of overstress in bracing or wall timbers, or both, during sinking.

The great advance in the design of the walls of the Delaware River Bridge caissons was in making them self-supporting, thus freeing the working chamber of the obstruction of cross-ties and braces. The four bulkheads which divided the working chamber into five compartments were provided only for support of the caisson during sinking and did not brace the side walls. The change to steel design permitted the use of steps in the inner face of the caisson wall and made the actual cutting edge itself more accessible.

Even without bracing in the interior of the working chamber, the toes of these caissons were much stronger than those of most

TABLE II.

Comparison of Strength of Caisson Working Chamber Walls.

Caisson.	Outward thrust per foot in lbs.	Inward thrust per foot in lbs.
Quebec Bridge (1910)	2,000	26,000
Manhattan Bridge	5,000	36,000
Metropolis Bridge	7,000	87,000
Delaware River Bridge	55,000	70,000

of their predecessors. Table II gives the thrust in pounds at the cutting edge, which each of several notable caissons would have resisted at safe working stresses, per foot of working cham-

ber wall, or toe. It will be noted that the Delaware River Bridge design is the only one which has a toe almost as strong against outward as inward thrust.

Bulkheads similar to those used in the Delaware River Bridge caissons had been employed in the Quebec Bridge caissons with satisfactory results.³ They make it possible to carry the entire weight of the caisson and the completed portion of the pier on bearing under these bulkheads instead of on the cutting edge as would otherwise be necessary. This is a great advantage in controlling the sinking and in carrying the caisson through heavy boulders or into rock, without damage to the walls of the working chamber.

Another unusual feature of these caissons, required by the specifications, was the emergency chamber, located above the roof of the working chamber in the mass concrete. This was planned to serve as a place of refuge for the entire shift, in case of blow-out or other accident in the working chamber, until the men could be locked out. It had access to each of the five compartments of the working chamber by separate manholes through the roof, each provided with a ladder. It had its independent source of air supply but would have served as an air reservoir, on the principle of the diving bell, even in case of failure of the air supply. In actual use, fortunately, no emergency developed. The chamber nevertheless served a very useful purpose as a communicating gallery, by which the men reached the compartment in which they were to work without the necessity of passing through successive bulkheads. The emergency chamber clause was one of several in the specifications, inserted to safeguard the men working under air, the details of executing which were left to the contractor, subject to the approval of the engineer. Another was the provision at the refuge chamber level of emergency locks, capable of holding an entire shift at one time. A stairway in a water-tight open shaft led from these locks to the surface.

What was planned to be the regular service man lock was above water, at the top of a four-foot shaft, which was equipped with an elevator hoist bucket. Actually the large tunnel

³ The pump pit caissons for the waterworks of the City of Cincinnati, built in 1898-99, used a number of cross-bulkheads designed with cutting edges, but changed to act as bearing walls only. . . . the first definite use of cross-walls as carrying walls pure and simple.—*Memorandum by Daniel E. Moran.*

locks, which were installed just above the roof of the working chamber as the emergency locks, were used and this elevator hoist neglected.

The contract drawings for the caisson showed typical cofferdam sections, designed so that they might be detached from the caisson proper on completion. On the western rivers, the masonry of the pier shafts is quite commonly started before the caisson is sunk to its final elevation, and laid as fast as sinking progresses, so as always to keep the top of the masonry above water. With this practice no cofferdam is needed, except possibly until the caisson is firmly landed. On the Delaware River Bridge work the contractors preferred to complete the sinking before starting the masonry, thus insuring that the pier shafts would be exactly in correct position without any offsetting of the masonry courses and also that only the minimum amount of granite masonry would be required. They accordingly provided sufficient cofferdam to reach from the top of the caisson proper to above high water level. Only the top section, above the level of the bottom of the granite-faced portion of the pier, was made removable. The others were narrowed up, so as to act also as forms for the concrete portion of the pier shaft, and were left in place. The Camden caisson had 33 feet of cofferdam, left in place, and a 15-foot removable section.

The care given to the design of the caisson and preparation of the specifications probably deserves to share credit with the skill and experience of the construction organization for the smooth and rapid manner in which the actual field work went forward. The behavior of the caissons under the test of launching and sinking was a source of satisfaction to all those of the engineering staff of the Joint Commission who had had a part in their design.

II. CONSTRUCTION.

BY

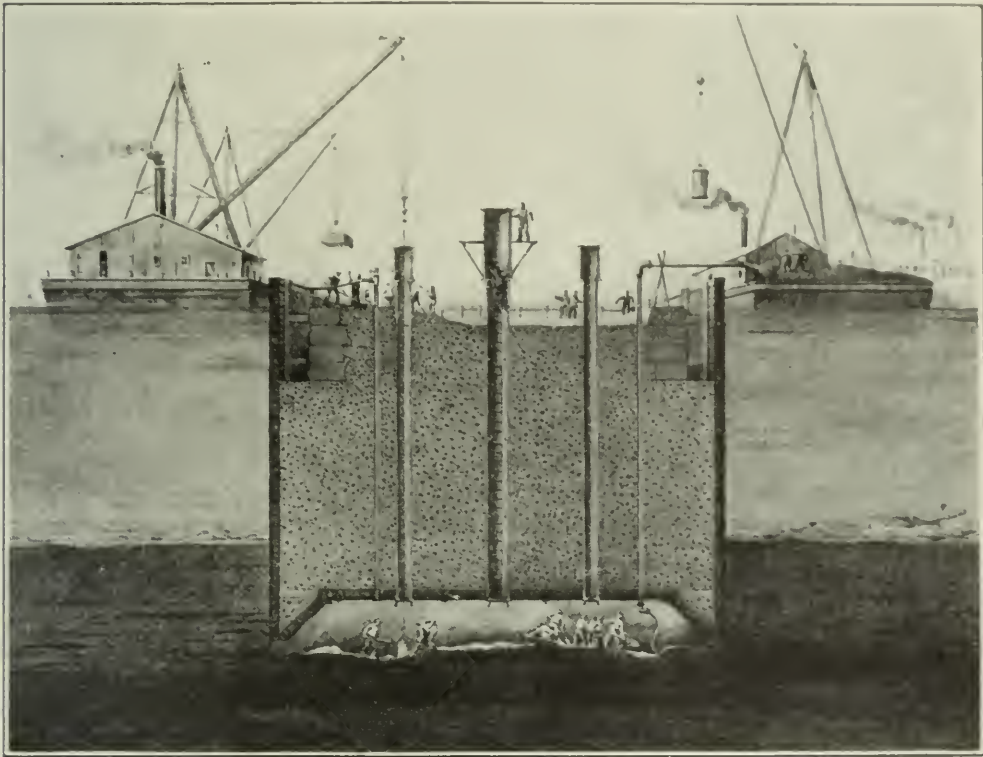
MONTGOMERY B. CASE, B.Sc., M.A.Soc.C.E.

Senior Resident Engineer, Delaware River Bridge Joint Commission.

At most locations where deep pneumatic bridge piers are to be built, one of the first problems is the selection of the method of supporting the caisson during construction and of launching it after it is ready to be floated.

This problem is frequently complicated by a considerable range in the stage of the water. At many locations on the Ohio, Mississippi and Columbia Rivers this range amounts to as much as 40 to 60 feet. Under such conditions the length required for inclined launch-ways, where the banks are flat, often makes their cost prohibitive, unless there are a number of caissons to be launched. Caissons of moderate size have been floated by means

FIG. 1.



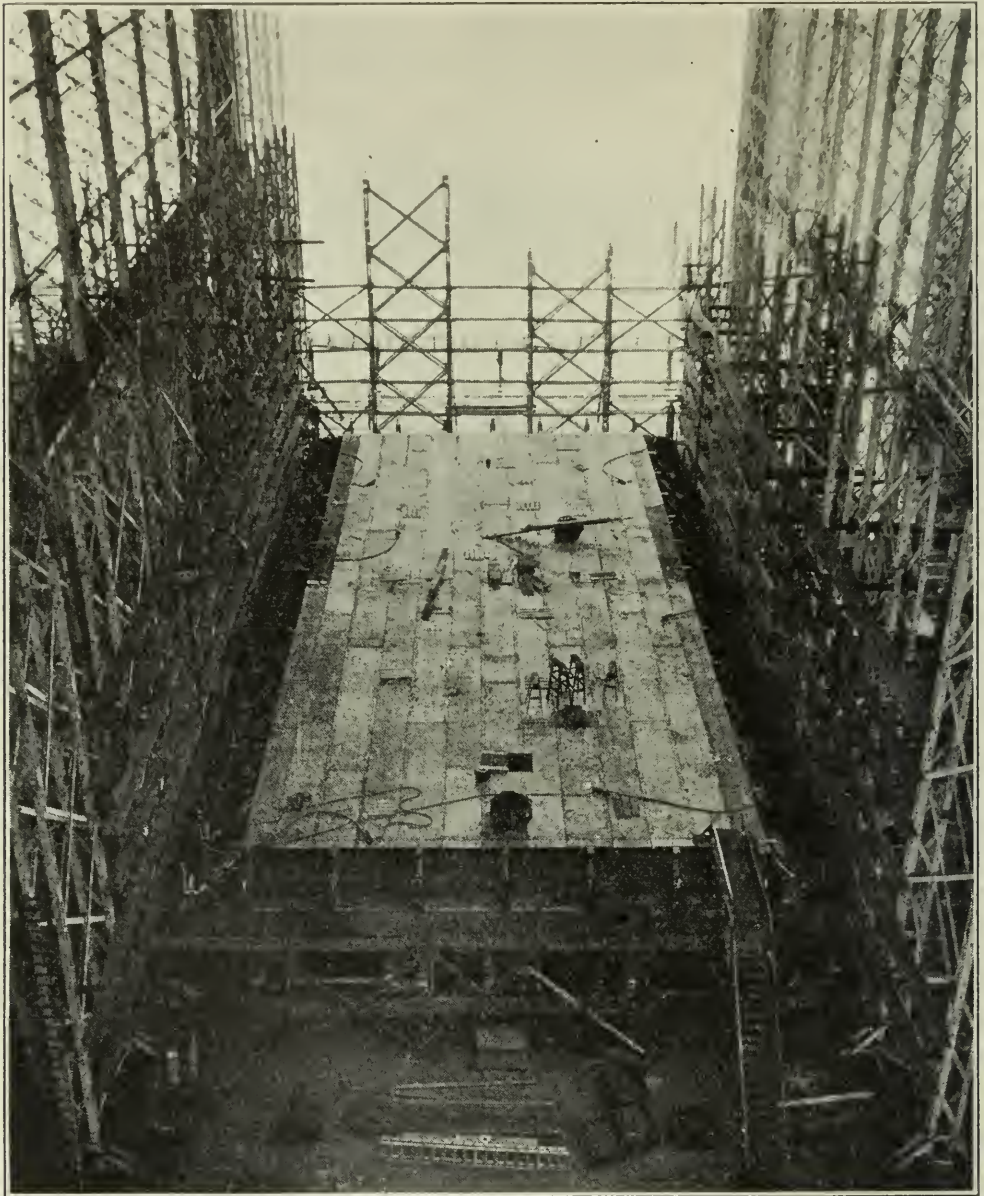
Sketch of typical pneumatic caisson foundation.

of lowering on large screws suspended from trusses supported on barges alongside the caisson. Larger caissons have been floated from pontoons built on the style of a primitive floating dry-dock. For piers near the bank or in shallow water, the caisson is sometimes supported during construction by filling the site to an elevation above the water surface and later sinking the caisson through this supporting fill.

For the piers of the Delaware River Bridge, it was fortunate to have several large shipyards with launch-ways capable of supporting a battleship, in close proximity. The plant and experi-

enced personnel were also a large factor in greatly reducing the cost and the time necessary to construct the caissons and launch them ready for sinking.

FIG. 2.

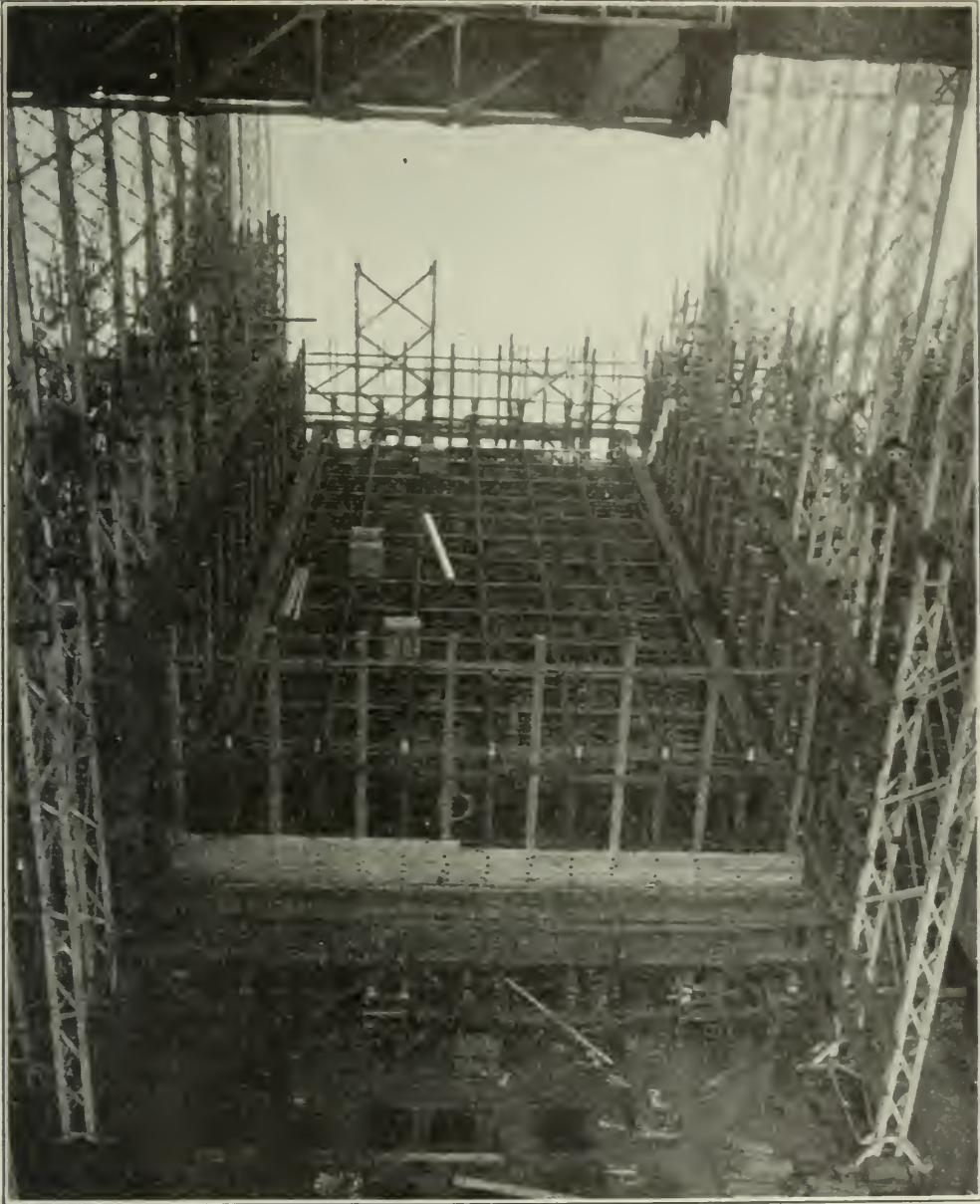


Side wall and roof plates in place on the building ways.

The adopted design, described by Mr. Chase in the previous paper, with steel cutting edges and steel-plated sides and with the roof of the working chamber supported by steel roof trusses, was in effect merely an inverted steel barge with a timber struc-

ture or crib rising above the chamber (Fig. 2). This construction lent itself admirably to the plant, tools and experience of a shipyard. The contractors for the two main piers of the Delaware

FIG. 3.

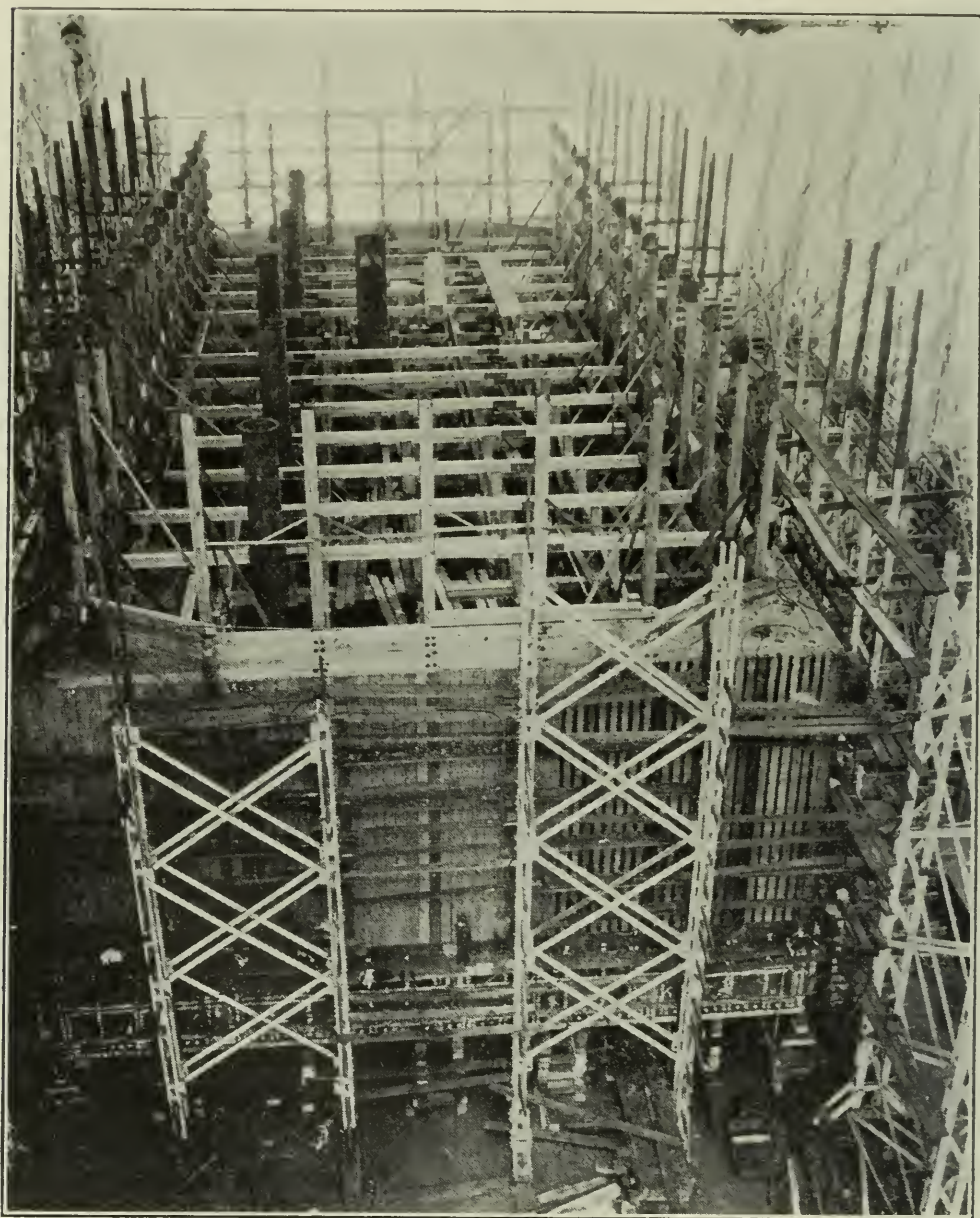


Caisson B showing $6\frac{1}{2}$ courses wall timbers in place.

River Bridge, Holbrook, Cabot and Rollins Corporation, of Boston, and the Keystone State Construction Company, of Philadelphia, acting jointly, selected the New York Shipbuilding Corporation to construct the caissons.

The fact that these caissons could be constructed to their finished height (Fig. 5), ready for sinking to their final depth, before they were launched, was in striking contrast to most situa-

FIG. 4.

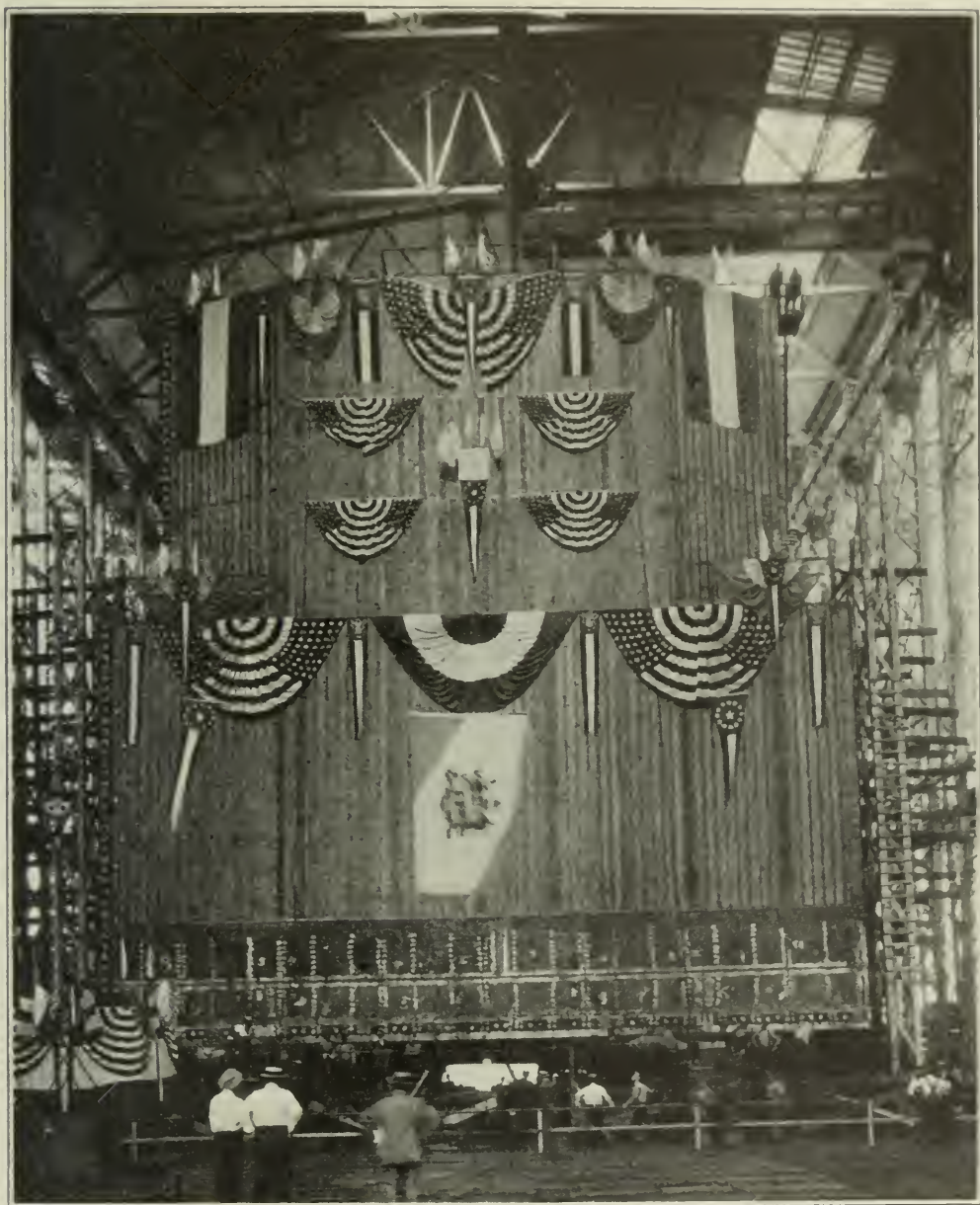


Caisson B erection progress.

tions, where the crib or structure above the working chamber is built up as the sinking proceeds. The rate of sinking is often limited by the rate at which the crib can be built up to keep it

above the water surface. The construction of the crib during sinking operations also adds materially to the complication of carrying on so many operations in a limited space.

FIG. 5.



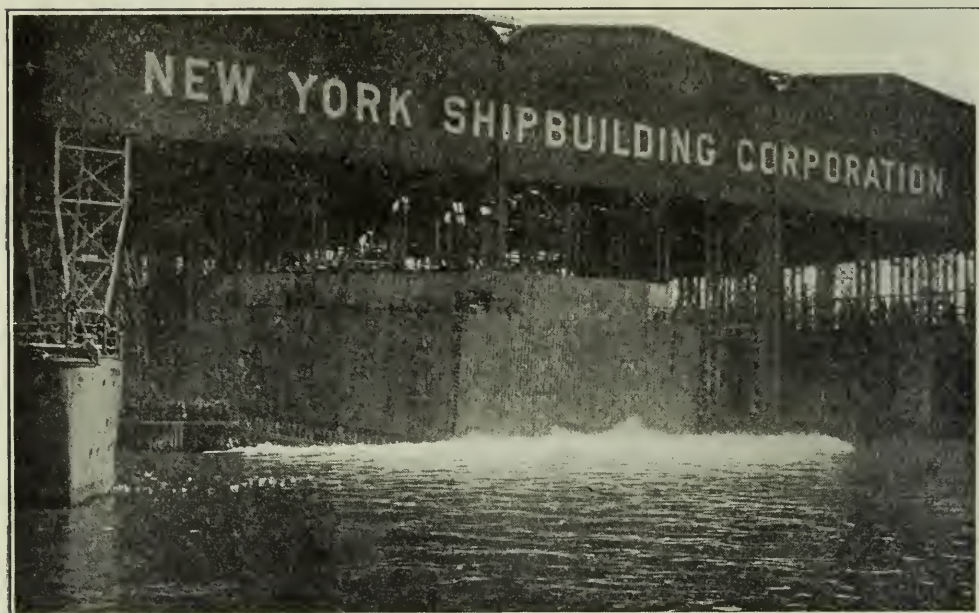
Caisson B ready for launching.

While the caissons were being constructed at the shipyard the sites of the piers were dredged to a depth of forty feet below mean high water. This excavation, even with the larger quanti-

ties involved in the side slopes, could be made more cheaply by dredging than by excavating the smaller volume within the area covered by the caisson under air pressure. This procedure was also an advantage, but such a method could not be used on many rivers with a swifter current and a shifting sand bottom where the dredged excavation would be filled by the current before the caisson could be settled on the bottom.

The plant provided for sinking the caissons was almost identical on the two sides of the river, but arranged somewhat differently

FIG. 6.



Launching of caisson A.

to meet the local conditions. On the Philadelphia side the plant was all located on the river end of Pier No. 11, North Wharves (Fig. 13). Six compressors, with a total rated capacity of 5000 cubic feet of free air per minute, were provided. One of these could be operated as a high-pressure machine to furnish pneumatic power for the rock drills in the caisson. Six one-hundred horsepower boilers were provided, which also furnished steam for two one-yard concrete mixers, hoisting engines, pumps and other auxiliary machines. Air was carried from the receivers to the caisson by two four-inch and two six-inch pipe lines, laid along two independent routes. Every pipe line entering the caisson working chamber was protected by a gate valve where the

line left the dock, and in addition to this the air supply lines were provided with a check valve at the top of the caisson and with a clapper valve at the roof inside of the working chamber.

While the five compartments formed by the four bulkheads were at all times interconnected by the two open passages through the bulkheads and by the clear working space along the cutting edge at the ends of the bulkheads, the precaution was taken of having one of the air supply lines enter each of the compartments

FIG. 7.



Towing caisson B into position.

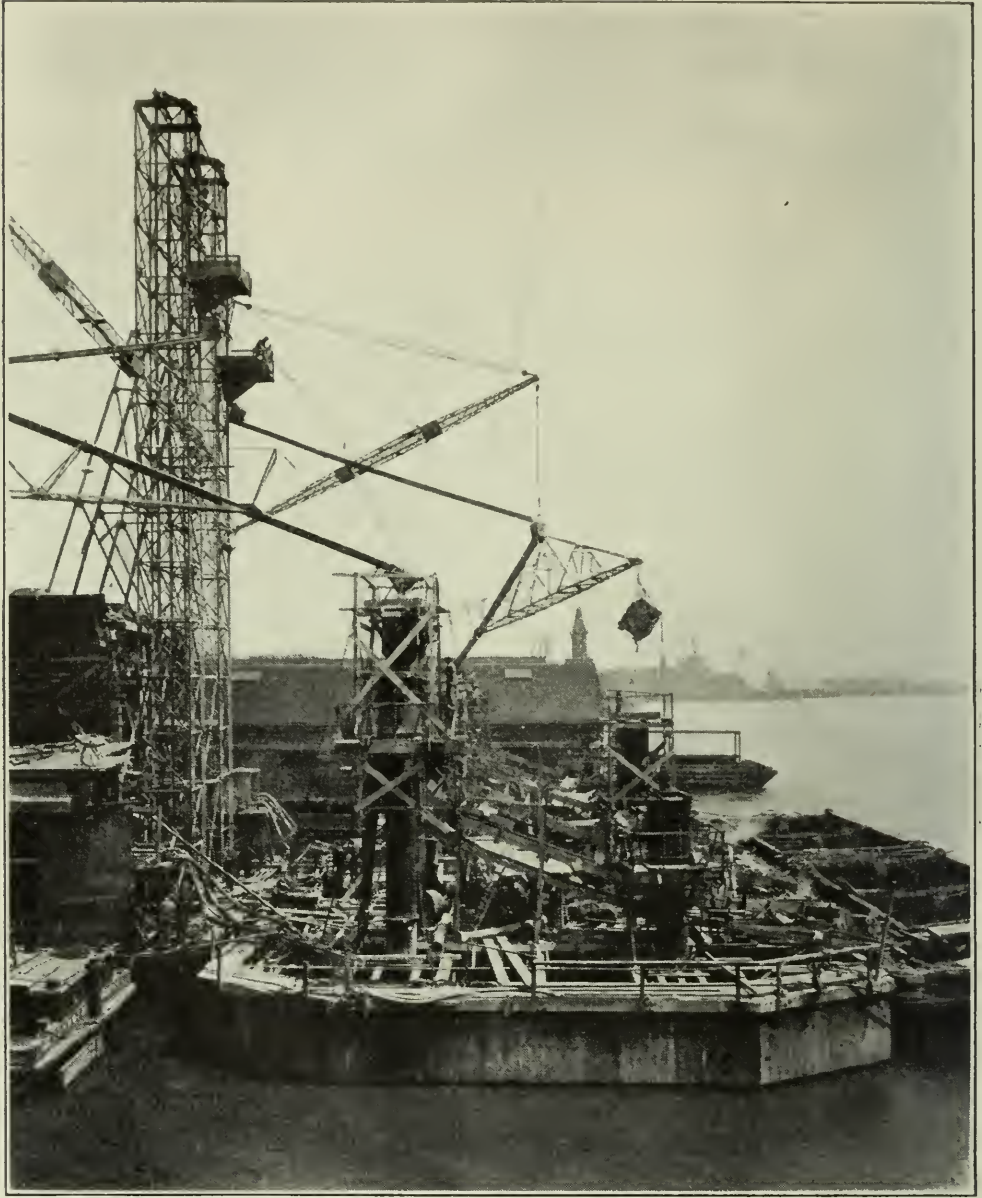
except the centre one. An air supply was provided just above the roof of this compartment in the refuge passage at the inside door of the man locks.

These conditions were the same for the caissons on both sides of the river. The principal difference in the arrangement of the plant on the two sides of the river consisted in the location of the compressors in Camden back at the street line, some fourteen hundred feet from the caisson. The towers for hoisting concrete were at the end of the caisson on an adjoining pier (Fig. 11), requiring somewhat longer distributing chutes than in Philadelphia, where the concrete towers were on the end of Pier No. 11 near the centre line of the bridge.

When the caissons were launched they weighed about 1800

tons and drew twelve and one-half feet of water. The site having been previously dredged to a depth of forty feet below mean

FIG. 8.



Caisson A in permanent position, view from Pier 10. The lock on the right is handling muck, on the left the hoisting sheave has been removed and the concrete lock applied preparatory to sealing.

high water, it was possible to sink the caisson twenty-seven and one-half feet by the addition of concrete load before the cutting edge came in contact with the river bed.

This loading permitted a depth of twelve feet of concrete in the crib over the roof of the working chamber and brought it to within three feet of the top chord of the steel stiffening trusses.

FIG. 9.



Pier A, looking north, showing method of handling granite.

This reinforced concrete slab, in addition to the trusses, thus made it possible to obtain considerable rigidity against warping while the caisson was still floating. Before air pressure was applied, which increased the flotation by the displacement of the

water in the working chamber, it was possible to bring the concrete over the top chord of the trusses, thus insuring a very rigid structure to resist the forces set up by the bearing on the bulkheads and cutting edge.

On the Philadelphia side this condition of approximate equilibrium was maintained at most all stages of the sinking so that

FIG. 10.



Pier A, southern end, showing granite construction.

the caisson structure was at no time called upon to carry any great load at the cutting edge. In fact, on three occasions, when the daily computations of load and reactions were made, it was found that there was a positive uplift, in one case of one hundred and fifty-six tons at high tide. This uplift was either resisted by the friction on the sides of the caisson or may not have actually existed, since the gross weight of the caisson was at this time in excess of 17,000 tons and an error of less than 1 per cent. in the assumed unit weights or the recorded quantities would account for the difference.

With a tide of five or six feet,* the cutting edge necessarily

came to bearing several times before sufficient concrete could be placed to hold the caisson down at high tide. This made the mooring in accurate location more difficult, but when the Philadelphia caisson was firmly on bottom the position of the upstream end was two inches west of true position, the downstream end was one foot east, and the centre was four inches upstream from the bridge axis. During sinking this location was changed to a

FIG. 11.



Caisson B from Stockham wharf, showing Matison muck locks in place. The muddy streaks are from the blowpipes.

skew of eight inches at the time of sealing, which was well within reasonable tolerance for a caisson $70' \times 143'$, and offered no difficulties in placing the granite masonry on correct location within the cofferdam. The cutting edge was eight inches out of level across the diagonal and at an average elevation -60.65 . The datum plane used is that of the City of Philadelphia, which is 2.43 feet above mean high water in the Delaware River, as determined by the United States Engineer Office.

The Camden caisson was grounded with the upstream end on true position, the downstream end was two inches east of position and the caisson was less than one inch upstream from the centre

line. The cutting edge was less than eleven inches out of level across the diagonal. When sunk to final position the location at the base of granite was correct at the upstream end, three and one-half inches east at the downstream end and one and one-half inches upstream from the centre line. The cutting edge was four

FIG. 12.



Pier A, looking northeast, Philadelphia side.

inches out of level across the diagonal and at average elevation -84.83 .

No objectionable warping of the plane of the cutting edge or distortion of the side walls of the working chamber was found at any time during the sinking of the Philadelphia caisson. The Camden caisson was, therefore, handled with considerably more load which assisted in speeding up the excavating and sinking, in that the trenching along the cutting edge was less tedious. The general practice followed was to carry the net weight or unbalanced load on pillars of undisturbed material under the bulkheads. After mucking had progressed to a point where the caisson ceased to follow down, the pillars were robbed and reduced in area so that they would crush and permit the caisson to settle.

Most of the excavated material was removed from the working chamber by hoisting in buckets through the muck shafts (Fig. 1). Some sand and gravel were blown out through the six-inch pipes. This operation is accomplished by feeding a mixture of water, sand and air into a flexible but non-collapsible hose which is attached to the pipe at the roof line. If the operator allows the lower end to remain constantly submerged, a solid column of

FIG. 13.



Aerial view both sides of river.

water and sand is fed into the pipe which, being no lighter than the hydrostatic head, balanced by the caisson air pressure, the water column soon comes to rest and the solid material, settling back, plugs the pipe. On the other hand, too much air fed into the pipe is wasteful of power, reduces the rate of discharging excavated material, and in extreme cases would result in lowering the caisson pressure sufficiently to cause a premature settlement.

In the hands of an experienced operator the blowpipe is by far the most rapid and economical method of removing sand or gravel. Stiff or hard clay and broken rock must be locked out through hoisting shafts.

Each of the ten three-foot diameter muck shafts was equipped with a Matison type lock which proved very efficient (Fig. 8 and Fig. 11). These locks have the upper door opening in the cylindrical shell of the lock. The door is hung from a track riveted around the circumference of the top of the lock above the door opening. The door is curved to the same radius as the shell of the lock and is rolled open or shut like a barn door by means of a countersunk handle in the outside face of the door. The lower door is hinged and is swung up into a horizontal plane by means of a lever on the hinge shaft which passes through a stuffing box. Both doors seal on three-eighth inch rubber packing. Thicker packing is not desirable because it would expose a greater edge area to the pressure, and experience has shown that it more frequently blows out from under the packing ring or the contact surfaces between the door and the seat. The hoisting cable passes up through a packing gland centred over the hoisting shaft in the top of the lock. When the fourteen cubic-foot bucket of clay is hoisted up from the river bed, at the bottom of the working chamber, into the lock, the bottom door is swung up under the bucket, the air pressure is released from the lock into the atmosphere and then the pressure being relieved on the upper door, it can be rolled open and by slacking on the hoisting line the bucket of muck is dumped out through the door into the chute which carries it overboard into a barge for disposal.

The bed rock surface was very sharply defined under the Philadelphia pier and is a mica schist with strata upset at an angle of 60 degrees with the horizontal. The surface was generally level along the east side of the caisson. Along the west side, the rock sloped down from one foot below the cutting edge at the southwest corner to eleven feet at the northwest corner. Careful soundings showed that the rock surface was not below this depth at any point. To avoid the larger volume of rock excavation it was decided to underpin the west cutting edge with a concrete wall down to rock without sinking the caisson further. This underpinning was done by trenching in ten-foot alternate sections longitudinally and in about three-foot depths vertically, so that at no time was more than a three-foot height exposed to air leakage or possibility of a blow-out. The additional precaution was taken of packing the exterior face of the trench with stiff plastic clay as rapidly as the sand was exposed. The operation was entirely

successful and the balance of the rock surface could then be cleared off, ready for sealing the working chamber with concrete.

Very little of the surface of the rock was disintegrated enough to require removal. The maximum depth of rock excavation on some of the high points was about eight feet. Drilling and blasting was carried on without difficulty. At the time of blasting the electric light cords were taken up into the refuge passage by the crew, who remained in the passage under the air pressure without locking out.

The sealing of the working chamber was accomplished by locking concrete in through the muck shafts. This required 3200 cubic yards of concrete. It was not sent down in buckets, but allowed to fall from the bottom door of the concrete locks.

These concrete locks were installed by removing the top ring on the muck locks, which ring carried the hoisting sheave and packing gland (Fig. 8). The concrete lock was then bolted in place through the same holes that had been used to bolt the top ring. The top door of the concrete lock was hinged and swung up into a horizontal plane by means of a hand line. The bottom door was also hinged and swung into a horizontal plane across the eighteen-inch bottom opening of the concrete lock. In operation this bottom door was handled by a man who entered through the side door of the muck lock and worked his shift under pressure. His duty was to clean the packing gasket after each batch of concrete and, after lifting the door, to signal for the lock to be equalized out for the next batch.

After the concrete had been brought up to within four feet of the roof, the precaution was taken of concreting through both shafts in the same compartment simultaneously. All pipes entering through the roof were cut off flush so as to avoid air pockets along the ceiling and as the concrete surface approached the ceiling these pipes were occasionally blown to relieve any air pockets and permit the concrete to flow towards the pipes located in the corners of the compartment. Grouting operations, after the sealing was completed and the caisson pressure removed, showed that the sealing was entirely successful.

The Philadelphia pier was sealed with the cutting edge at elevation -60.65 when the immersion at high tide was fifty-eight feet and the air pressure was twenty-eight pounds per square inch. The gross weight of the caisson was 20,000 tons.

The sinking operations on the Camden pier differed principally in the nature of the material passed through and the greater depth. Between elevations -52.0 and -63.0 an eleven-foot stratum of hard blue clay was passed through. Underlying this the material changed gradually to sand and gravel, then to sand, mica and clay, and then to a mica schist, which was disintegrated. This material increased in hardness gradually until rock was encountered which could not be removed without blasting, and which was satisfactory for the foundation.

The Camden pier was sealed with the cutting edge at elevation -84.83 when the immersion at high tide was eighty-two feet and the air pressure was thirty-four pounds per square inch. The gross weight of the caisson was 30,500 tons.

A careful medical examination was made of all applicants for employment under compressed air. The men of the engineering staff who were assigned as inspectors under compressed air were also given the same rigid examination. A doctor was in constant attendance at the pier at all times while the caissons were under pressure. Bristol recording gages on the man locks greatly assisted in enforcing the rules laid down as to the rate of decompression in the locks.

The time required for locking out men was :

5 minutes from 15 pounds pressure,
10 minutes from 20 pounds,
18 minutes from 30 pounds,
and 25 minutes from 35 pounds.

The lock-tenders usually endeavored to release the last few pounds very gradually. An exception was made in the case of lock-tenders or workmen coming out to take tools or supplies into the lock where they returned immediately into the pressure. In this case they frequently came out in but a few minutes, but returned at once to the pressure.

The working period at pressures less than twenty pounds was eight hours in two shifts of four hours each with an hour intermission between shifts. From twenty to thirty pounds, six hours in two shifts with an intermission of three hours. From thirty to thirty-five pounds, two shifts of two hours each, with a two-hour rest period between shifts.

These regulations, in some cases, were slightly more con-

servative than the requirements of the industrial law of Pennsylvania or New York.

Great credit is due to the contractors for the success with which the work was carried out without a fatality from any cause and with a remarkably small number of minor injuries.

On the Philadelphia side there were 10,500 decompressions with only one case of bends for each 617 decompressions. On the Camden side there were 15,500 decompressions with one case for each 320 decompressions. The symptoms usually appeared in less than three hours after locking out and were relieved by recompression in the hospital lock, followed by a very slow decompression. The higher rate on the Camden side was probably due largely to a higher proportion of less experienced men who reported the symptoms when they appeared. The older men frequently conceal any light attacks to avoid possible loss of time if ordered off the shift. The higher air pressure carried would also be a contributory cause and is reflected in the record showing the largest number of cases at twenty-three pounds on the Philadelphia side and at thirty pounds on the Camden side.

A further probable contributing cause was the smaller quantity of air per man used on the Camden side. The ten-foot clay stratum passed through on that caisson served to act as a tight seal reducing the amount of air passing under the cutting edge. On many occasions when the locks were not in active operation the precaution was taken of opening vent pipes to insure a larger quantity of air for ventilation. While the plant was not equipped with meters, a careful estimate from the compressor operating records indicate that about twenty-two cubic feet per man per minute was supplied on the Philadelphia side, while on the Camden side the maximum was about sixteen cubic feet, the minimum twelve cubic feet, and under average conditions the air supply was fifteen cubic feet per man per minute. These quantities are quite approximate.

Temperature Coefficient of the Refractive Index of American Turpentine. GARTHA THOMPSON (*Analyst*, 1922, 47, 469) has determined the temperature coefficient of the index of refraction of authentic samples of American turpentine, using sodium light and the Pulfrich refractometer. The coefficient ranged between 0.000468 and 0.000470.

J. S. H.

The Recording Ultra-micrometer. J. J. DOWLING. (*Phil. Mag.*, July, 1923.)—"It will, of course, be understood that an apparatus which records small capacity variations will be immediately suitable for measuring minute movements, inasmuch as the capacity of a condenser varies with the separation of the plates." A condenser is joined to an oscillating valve circuit. If it is composed of two circular discs 5 cm. in diameter, separated by a distance of .025 cm., then a change in the distance between them of $1/10,000$ cm. should produce a change in the anode current of 8 micro-amperes. A galvanometer joined in a special manner should show a deflection of 800 divisions for this current.

The instrument has found application in several cases. The two condenser plates, circular discs, 10 cm. in diameter, were clamped to a steel rod, 12 mm. in diameter, passing through their axis. When weights were placed upon the rod, it was compressed and the distance from the clamp supporting the upper plate to that supporting the lower was made less. This distance was initially 5 cm. The addition of 2 kg. produced a deflection of 121 divisions on the galvanometer. From the elastic constants of the steel it is found that one such division corresponds to one ten-millionth of a centimetre. The promptness with which the apparatus responds to the application of forces tending to change the distance from plate to plate was tested by using it to record the growth of the root-tip of a plant. The lower plate was rigidly supported, while the upper one was carried by a spring. The root-tip growing downward pressed upon it and moved it nearer to the lower plate. "The growth pulses noticed by Bose are shown very convincingly."

Again, one condenser plate was held in a horizontal plane by a spring stretched by a weight of 1 kg. hung from it by a silk cord passing through a hole in the lower plate just beneath. When 50 kg. of lead were brought near to the suspended kilogram the gravitational attraction pulled the movable plate down far enough to make the galvanometer deflect through 300 divisions, though the displacement was of the order of one eight-millionth of a centimetre.

The author is engaged in studying rapidly changing stresses in machinery with the aid of the instrument he has devised.

G. F. S.

Complex Cyanides. GEORGE JOSEPH BURROWS, of the University of Sydney (*Jour. Chem. Soc.*, London, 1923, 123, 2026-2029), has studied the cryoscopy and conductivity of aqueous solutions of sodium ferrocyanide, potassium ferrocyanide, potassium ferricyanide, potassium cobalticyanide, and potassium chromicyanide. The results indicate that each of these salts yields cations of the alkali metal and a complex anion containing six cyanogen groups and an atom of either iron, cobalt, or chromium. This anion may undergo further electrolytic dissociation into simple cyanide anions and a metallic cation.

J. S. H.

IONIZATION AND RESONANCE PHENOMENA.*

BY

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THE quantum theory of radiant energy, which was originated by Planck in 1900 in an attempt to explain the distribution of energy in the spectrum of a completely absorbing body, has since that time been extended to cover an important fraction of the entire field of physics. This theory which postulates that energy in the form of radiation is not continuous in structure but is made up of discrete bundles or quanta each of magnitude $h\nu$, where h [†] is a constant and ν is the frequency of the radiation, has been applied in two main fields. The first of these fields is the field of black-body phenomena, atomic heats and the kinetic gas theory. The second field is that covering the interaction of radiation and matter—both the stimulation of radiation from matter through the impact of electrons on it and the stimulation of the electrons of matter by the absorption of radiation in it. Research in the second field has been especially successful in throwing light on the structure and on the dynamics of the atom. This paper deals with certain subjects lying in that second field being concerned mainly with the interpretation of the theories of spectrum production and absorption.

The first successful application of the quantum idea in the study of spectra was involved in Bohr's theory of atomic structure and the mechanism of radiation which was published in 1913.¹ In order to introduce our subject properly it will be necessary to summarize briefly the main points of that theory. It will be recalled that Bohr developed Rutherford's idea that atoms consist of aggregations of positive and negative electricity—an exceedingly minute nucleus with a net positive charge equal to its so-called atomic number being surrounded by a sufficient number of negative electrons exactly to neutralize it in the normal state. These electrons are supposed to move about the nucleus in paths

* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute, held Thursday, March 8, 1923.

[†] h equals 6.554×10^{-27} ergs seconds.

consistent with the laws of classical mechanics with this vital and as yet unexplained exception that an electron moving in a fixed configuration loses no energy by radiation. Further, it is assumed that only such particular states of motion are possible in which the angular momentum of the electron about the nucleus is some integral multiple of $h/2\pi$. As a consequence of these assumptions the energy of any particular system of motion, that is a system with fixed radii of electronic orbits and an angular momentum equal to $nh/2\pi$, is invariable, and energy can be given out or absorbed by an atom only through a swelling up or shrinking down of the system from one stationary state to another. The fundamental idea of the Bohr emission and absorption theory may consequently be stated as follows: The energy radiated or absorbed by an atom in passing from one stationary state to another equals the difference of the energies in the two states, $W_2 - W_1$, and is in all cases equivalent to one quantum, $h\nu$, of monochromatic radiation of frequency ν .

For an atom having one electron only, the energy, W , of a particular state is easily found to be represented by $W = -2\pi^2 m_0 e^2 E^2 / h^2 \times 1/n^2$ where m is the mass of the electron and e its charge. E represents the positive charge on the nucleus and n is the integer showing which multiple of $h/2\pi$ represents the angular momentum of the electron in the particular state considered. This n clearly specifies the successive possible orbits which the electron can occupy and is consequently frequently called the "orbit number." From this energy expression we may write, since $h\nu = W_2 - W_1$, $h\nu = -2\pi^2 m_0 e^2 E^2 / h^2 (1/n_2^2 - 1/n_1^2)$ to represent the energy radiated when the atom passes from one stationary state to another. This last formula may be written $\nu = NZ^2 (1/n_2^2 - 1/n_1^2)$ in which N is the Rydberg constant* and Z is the atomic number ($E = Ze$). The series of possible frequencies to be obtained from a simple atom of this sort is given by taking different combinations of the n 's representing the electron jumping between the corresponding orbits. These frequency values will also represent the radiations which can be absorbed by the atom. This formula ought consequently to express the successive lines in the bright line spectrum and also in the absorption spectrum of an atom which has a single electron. As a matter of fact the formula, being identical with the famous Balmer formula, does

* Rydberg's constant is 109,737.7 for a heavy nucleus.

give the lines of the hydrogen spectrum with extraordinary accuracy. It will be observed that the frequency of each line in the spectrum is here given by the difference of a pair of quantities which are determined by the energies of particular orbital motions and that with, for example, ten such quantities we could predict, speaking generally, some forty-five lines.

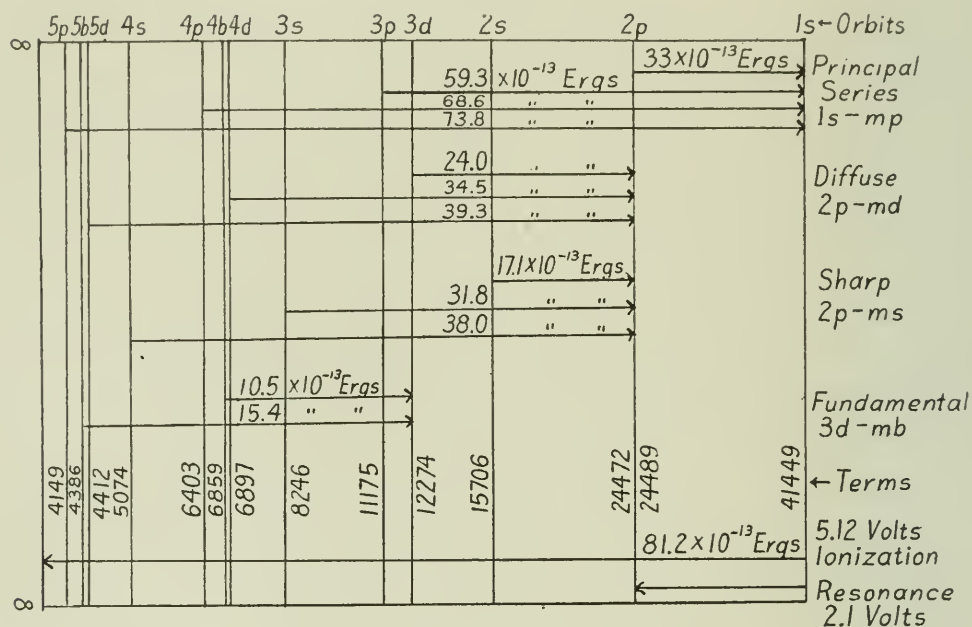
Let us next consider the formulas which have been developed from Balmer's formula by the spectroscopists for exhibiting the relations of the lines in spectra. When a fairly complex spectrum such as that of an alkali metal is examined, we observe certain series of more or less regularly spaced lines which have common visual characteristics so that we can distinguish series of sharp lines, series of diffuse lines and so on. The four most important series of this sort in the spectra of the alkali and alkaline-earth elements are, in the order of importance, the Principal, Diffuse, Sharp, and Fundamental series. These lines may be singlets, doublets or triplets—the total number being very large. It was found, years before Bohr's theory was thought of, that the frequencies of all these series lines could be expressed by differences between a much less number of other frequencies, not representing lines, which are called "terms." These terms can be calculated from expressions of the form $\nu = \frac{N}{(m+a)^2}$ where N is a universal constant, the Rydberg constant, m is given successive integral values to get the successive terms and a is a fraction which is constant for a given series and different for different series. The value of a is calculated from the observed lines. In the four important series just mentioned a is specified by P , D , S and F , respectively. The first term of the sharp group would thus be $N/(1+S)^2$ and similarly $N/(4+D)^2$ would be the second term of the diffuse series. These are terms, not lines. They are universally represented in an abbreviated form by the expressions $(1S)$, $(2D)$, and so on. To get the complete set of terms m , for S , is given all integral values from 1 up, for P all values from 2 up, for D all values from 3 up, and for F all values from 4 up. The frequencies of the lines making up the series of lines are given by taking differences of terms as follows:

Principal series	$\nu_P = (1S) - (mP)$
Diffuse series	$\nu_D = (2P) - (mD)$
Sharp series	$\nu_S = (2P) - (mS)$
Fundamental series	$\nu_F = (3D) - (mF)$

where the variable integer in the second part has always for its lowest value one more than the fixed integer in the first part.

These formulas actually predicted the frequencies observed experimentally, although at the time of their formulation it could not be explained why this should be so. The terms used in the formulas are frequencies which, by the use of the quantum relation, $W = h\nu$, can be converted into energy expressions. It is apparent that under the Bohr theory these terms can be taken to

FIG. 1.



Sodium Spectrum

represent the energies of particular orbital motions and that the formulas just written, known since 1896, can be taken to be equivalent to the Bohr formula $h\nu = W_2 - W_1$. We are therefore enabled to apply a definite meaning to terms like $2P$ or $1S$ or $3D$ as representing a particular possible orbit with a specific calculable energy. The orbit $1S$ always represents the condition of least energy, that is to say, it is the outermost occupied orbit of the normal or unstimulated atom.

Fig. 1, which represents the possible orbits of the sodium atom, will serve to illustrate these points. The centre of the atom lies well to the right of the figure. The outermost orbit occupied in the unstimulated atom is $1s$. The vertical lines parallel to $1s$ give the energy levels which may be occupied by an electron

ejected through an energy absorption from the $1s$ level. The values of the energy differences of the orbits in ergs and therefore of the energy absorptions necessary to bring about the corresponding transitions are given above the arrows and, at the same time, the "terms" of the series formulas are expressed on the orbit lines by their proper frequency values. The fundamental formula $h\nu = W_2 - W_1$ being accepted, it is immediately apparent, when we observe in the figure the possible transitions of the displaced electrons as represented by the arrows, why differences of terms give frequencies of emitted lines. The transition $1s - 2p$ shows the mode of development of one of the well-known sodium lines. The $2p$ level is a doublet too close to be shown as such in the scale of the figure.

The identification of these energy levels with the spectrum terms, introducing an enormous simplification into spectroscopy, is clearly a procedure involving an assumption of the validity of Bohr's theory. Any proofs which can be adduced supporting this identification will consequently serve equally well to support the notions of atomic structure and of dynamics which are involved in the theory. We shall now pass on to a consideration of the experimental evidences which can be obtained bearing on the energy absorptions and emissions actually associated with the production of spectral lines.

Two generally useful methods have been found by which measurable quantities of energy can be imparted to atomic systems, first, by striking the atoms with electrons which have fallen through a known difference of electrical potential and have therefore a known energy, second, by allowing radiant energy of known frequency, made up of quanta of known magnitude, to fall on the atoms.

Let us examine the first of these methods, that of electron impact. This method, of all that have been devised, gives the most direct proof of the Bohr idea and the one most free from theoretical elements. A metallic filament heated to incandescence emits electrons. Let us suppose that we have such a filament in a vacuum and that electrons are coming through its surface with zero velocity. Let us place near the filament a metallic grid maintained at a positive potential, V , with reference to the filament. The electrons will fall to the grid and there will be done on each an amount of work eV since V , the potential difference, is the

work done per unit charge and e is the magnitude of the charge. If the potential difference is one volt, *i.e.*, 10^8 e.m.u. of potential difference, the energy of the electron on arriving at the grid will be $1.59 \times 10^{-20} \times 10^8 = 1.59 \times 10^{-12}$ ergs—for a potential drop of 20 volts it would be 3.18×10^{-11} ergs. Since the erg itself is, as measured by our senses, an exceedingly small unit, these energy quantities may seem insignificant; however, let us compare them with the energies associated according to the quantum theory with various frequencies of radiation. The frequencies of red light and of blue light are respectively 0.38×10^{15} and 0.76×10^{15} . Since the energy quantum, ϵ , of any frequency is given by $\epsilon = h\nu$, where h is 6.55×10^{-27} ergs seconds, the quanta of these two radiations, red and blue, are seen to be 2.40×10^{-12} ergs and 4.98×10^{-12} ergs. These figures show that the potential energy developed by an electron in falling through even so small a potential drop as one volt is of the same order of magnitude as the quantum of red light. A simple calculation will show that a drop through 20 volts will give an energy equivalent to a quantum of radiation of wavelength 615 Å.*—very far down, indeed, in the extreme ultraviolet. Let us suppose that the space beyond the grid contains a certain number of atoms of a gas or vapor. The electrons which do not remain on the wires of the grid pass through and strike on the atoms. These atoms have electrons moving in concentric orbits about their nuclei and the electrons in the outermost orbit have, as we have already seen, a certain limited number of exterior orbits of greater energy in which it is possible for them to move. The atom is, according to these theories, incapable of absorbing any amount of energy excepting exactly such an amount as will throw an electron into one of the possible outer orbits. It happens, therefore, that when normal atoms are bombarded with electrons of gradually increasing velocity these will bounce off with undiminished energy until a certain critical velocity is reached at which they will suffer a definite loss of energy on impact. This loss of energy is the amount necessary to lift the atom-electron into its first exterior orbit; the equivalent potential is called the “resonance potential.” With still further increases in velocity new impact losses will develop in successive steps until a final value is reached at which the atom becomes ionized—that is, appears

* Å. represents the Ångstrom unit of length, namely, 1×10^{-8} cm.

definitely with a net positive charge. This energy value is that necessary just to remove an electron completely from the field of force of the atom; the equivalent potential is called the "ionization potential." The successive critical velocities at which energy losses occur correspond to the absorption frequencies of the atom as observed optically—dynamically they correspond to the energy content of successively larger exterior orbits. If the electron is free after displacement to spring back into its original orbit the energy absorbed in going out will be given up in coming back as monochromatic radiation and will be contributed to the strength of some line in the spectrum of the gas. If the bombarding energy equals or exceeds the ionizing energy so that all the exterior orbits are being occupied and vacated in different atoms at the same time the total emission will comprise all of the lines of the absorption series. If the ejected electrons are dragged away by an exterior field so that reëntry into the atoms is impossible, ionization alone occurs without any emission of radiation.

The limiting energy of the striking electron which just lifts the atom-electron out of the atom is called, as we have stated, the ionization potential. The highest frequency line in the absorption spectrum of the element, the ultra-violet limit, corresponds to this ionization potential—the first line in that spectrum, that is the lowest frequency line, corresponds to the resonance potential or potential of the first inelastic impact. Having either of these potentials, or any of the intermediate potentials of inelastic impact, the frequencies of the corresponding spectrum lines are given by the simple formula $cV = h\nu$, in fundamental units, or by $V \text{ (volts)} = \frac{12331}{\lambda(\text{\AA})}$ in ordinary units.

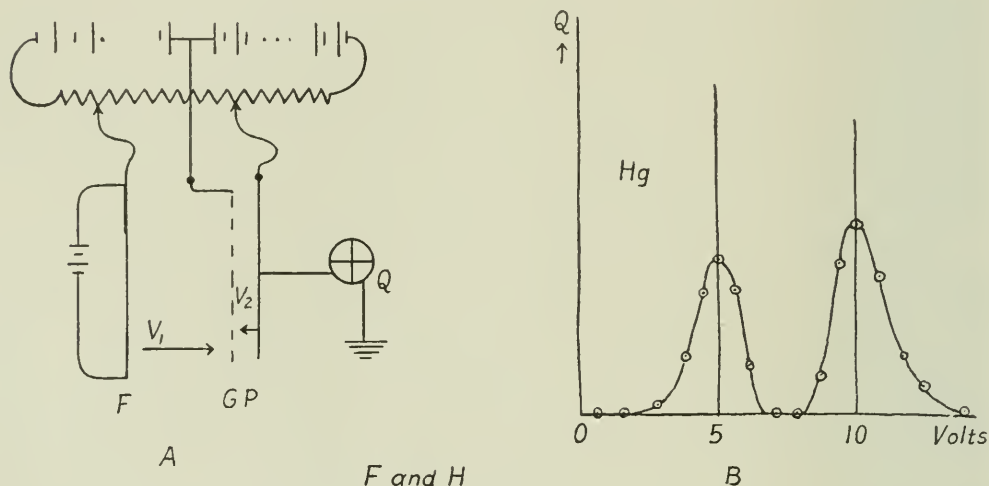
We have now before us the essential features of the phenomena of impact stimulation. The critical velocities of inelastic collision, including the ionization potential and the resonance potential as upper and lower limits, are seen to give us a direct measure of the energies of the atoms in certain of their stationary states. Studies of these velocities, therefore, furnish us with one of the most powerful means at our disposal for investigating the dynamics of atomic systems.

We shall next consider very briefly the methods involving electron impacts which have been used experimentally to determine these energy values. In the extensive literature of this subject a

variety of arrangements is described of which the two shown in Fig. 2 and Fig. 3 are typical.

Fig. 2 represents one of the original devices used by Franck and Hertz.² The electrons, developed from a hot wire, F , are accelerated to the grid, G , between which and the plate, P , a fixed retarding potential of a few volts is maintained. Suppose this retarding field to be three volts. As the accelerating potential, F to G , is gradually raised, no electrons can get to P until the driving voltage reaches three volts. The plate current registered by Q will then rise steadily as shown in the graph, B , until the energy

FIG. 2.

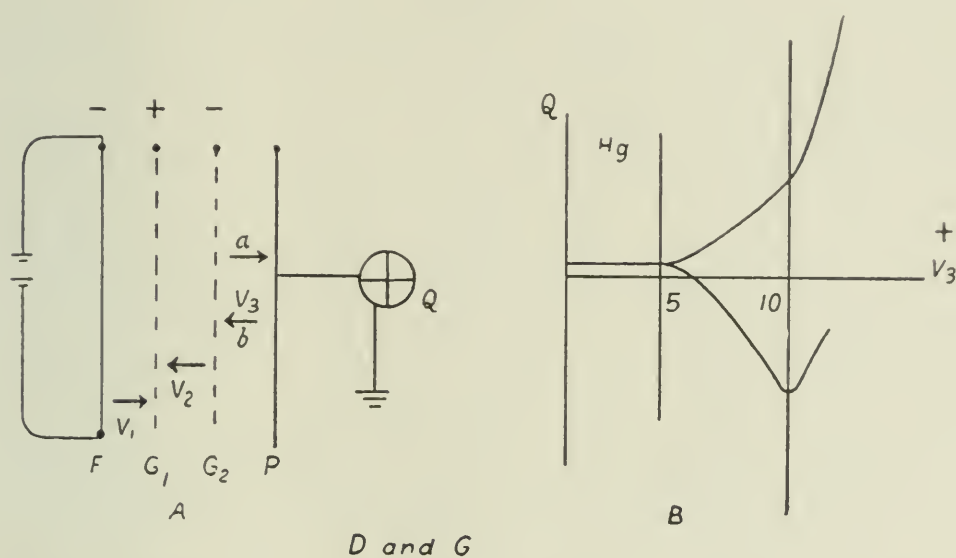


of the electrons striking the gas atoms in the plane of the grid is sufficient to lift atom-electrons from the outermost stable orbits of those atoms to the first possible exterior orbit. At this voltage inelastic impacts will occur between the electrons and the gas atoms. These inelastic impacts will reduce the velocity of the electrons to zero wherefore the current arriving at P will fall to zero and will remain at zero until the accelerating potential reaches a value three volts above the inelastic impact value. The plate current then rises as before until the electrons brought to rest in the first layer of inelastic impacts have, in falling forward from that layer, again acquired the critical energy necessary to throw the atoms into their first unstable state. At this point inelastic impacts will occur a second time and the plate current will again drop to zero and so on again if the accelerating voltage is lifted further. The potentials, F to G , at which the current in Q drops are clearly potentials of inelastic collision which may be either resonance

potentials or ionization potentials. The curve shown (Fig. 2*B*) is that for mercury vapor in which energy absorptions occur at five volt intervals.

Fig. 3 is a schematic diagram of an apparatus developed by Davis and Goucher³ to differentiate resonance potentials and ionization potentials, something not readily done with the simpler apparatus of Franck and Hertz. Here a second grid, G_2 , is introduced with arrangements whereby it may be made either positive or negative with reference to P . When the driving potential V_1 reaches a critical value inelastic impacts occur in the plane of G_1 .

FIG. 3.



If these impacts are resonance impacts radiation only will be developed without the liberation of atom-electrons and the production of positive ions. This radiation, falling on both G_2 and P , will produce a photo-electric emission of electrons from whichever one is negative with reference to the other; consequently a current will flow in whichever direction the field V_3 may be established. Reversing this field at each voltage reading will give, therefore, a double curve, such as is shown at *B* (Fig. 3), leaving the voltage axis at the resonance potential. When, however, the impacts have sufficient energy to ionize the atoms at G_1 , the liberated atom-electrons will be returned to G_1 , by the field V_2 , and, at the same time, the plus ions, that is, the positively charged atoms, will be carried across to G_2 . If, now, V_3 is directed as represented by the arrow *b* (which refers to

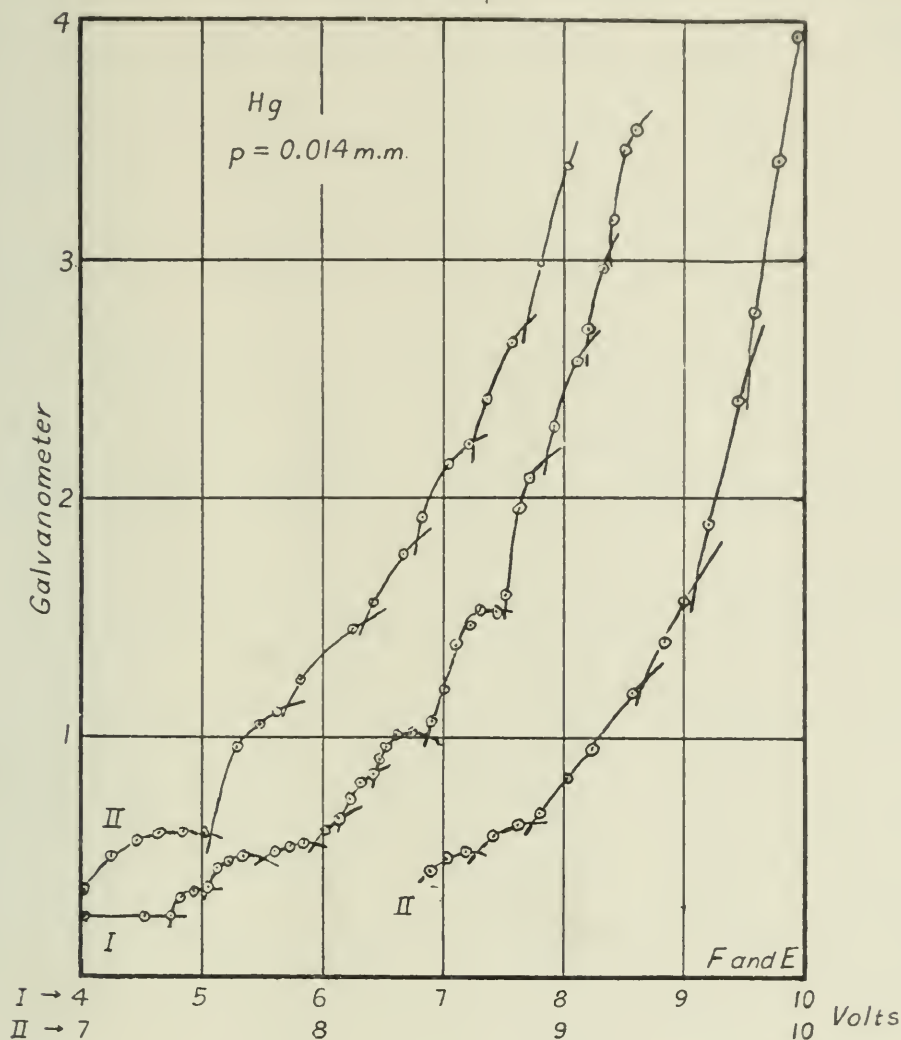
the motion of the electrons in the field) the plus ions will pass directly across to P and a positive current will be registered by Q . If, on the other hand, the field is set in the direction a but kept smaller than V_2 , then the plus ions will still cross to P and a positive current will again be registered. These positive currents added to the photo-electric currents, which still reverse with V_3 , give the upward breaks in the graph B which therefore clearly indicate the potential of ionization of the atoms.

In order to study the results obtained with such devices as those just described let us concentrate our attention on a single vapor, that of mercury—a vapor extremely suitable for such investigation because it is monatomic and because its atom is especially elastic, no energy losses other than those associated with changes in the atomic configurations being observable. The application of the method of Davis and Goucher to mercury showed inelastic impacts to occur and radiation to be produced at 4.9 volts and at 6.7 volts and inelastic impacts with ionization to occur at 10.2 volts. The quantum relation, $eV = h\nu$, applied to these voltages enables us to calculate that the radiations developed during the return of the atoms to their normal state after the corresponding energy absorptions ought to have wave-lengths 2537Å. and 1849Å. for the resonance points and 1188Å. for the ionization point. Franck and Hertz ⁴ conclusively established the presence of the first of these radiations by photographing it. At 4.9 volts stimulation the spectrum consists of this one line only. The other lines were not observed spectroscopically as they are absorbed by quartz. Evidence on the limiting short wave value of the spectrum, λ 1188, had previously been obtained, however, in an apparatus of a different character by Richardson and Bazzoni ⁵ who determined the maximum velocity of emission of the photo-electrons developed by radiation from a discharge in mercury vapor by curling them up into a circle of known radius in a magnetic field and found the length of the shortest waves from the arc to be not more than 1200 units and probably somewhat less—a result in good concordance with the value indicated by the impact method.

The early methods of investigation, such as those described above, could be depended upon to give the ionization potential and the resonance potential, that is, the point at which radiation is first developed and the point at which ionization occurs,

but they were apparently not capable of detecting all those intermediate energy absorptions which ought to be associated with the occupation of successive orbits below the ionization potential. In 1920 Franck and Einsporn⁶ succeeded in getting results with a method in which these successive potentials could be separated

FIG. 4.



by noting, under carefully controlled conditions, the successive rises in the photo-electric current from an electrode exposed to the radiation from the discharge. The results obtained by them using mercury are shown in Fig. 4. The breaks in the curves, which are curves of photo-electric current, indicate the potentials at which new radiations appear. A total of eighteen successive energy steps between the resonance potential and the ionization potential were determined although the final values do not all

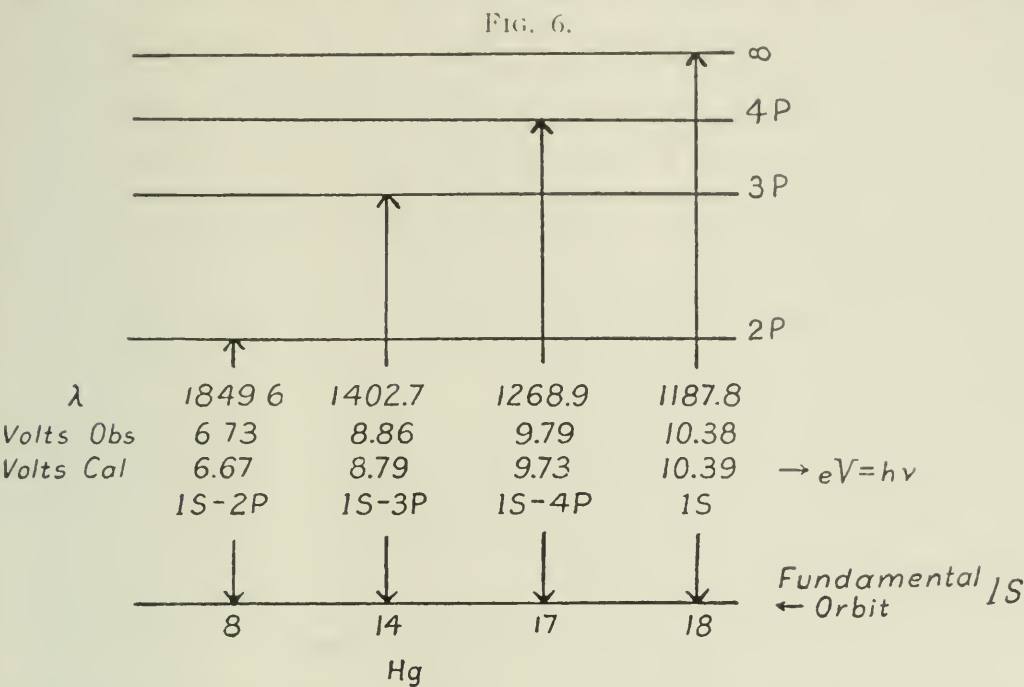
appear in the figure shown. The exact values are collected in the table (Fig. 5). Before the significance of the spectrum terms at the right of the table can be made apparent something must be said of the constitution of the mercury spectrum as determined

FIG. 5.

Number of Line.	Observed Voltage.	Wave-length.	Calculated Voltage.	Series-term.
1	4.68	2656.5	4.66	$1S-2p_3$
2	4.9	2537.0	4.86	$1S-2p_2$
3	5.32	2338	5.28	$1S-2p_1$
		2313	5.34	
4	5.47	2270.6	5.43	
5	5.76	2150	5.73	$2p_3$
6	6.04	(2043)		
7	6.30	(1958)		
8	6.73	1849.6	6.67	$1S-2P$
9	7.12	(1733)		
10	7.46	(1654)		
11	7.73	1603.93	7.69	$1S-1s$
12	8.35	(1446)		
13	8.64	1435.6	8.58	$1S-3p_2$
14	8.86	1402.7	8.79	$1S-3P$
		1400.0	8.81	$1S-3d_1$
15	9.37	2656.5	2×4.66	
16	9.60	1307.8	9.44	$1S-4p_2$
		2656.5	$4.66 + 4.86 = 9.52$	
17	9.79	2537	2×4.86	$1S-4P$
		1268.9	9.73	
18	10.38	1187.8	10.39	

by the spectroscopists. This spectrum is a complex one consisting of a set of singlets (single lines) and of a set of triplets which form combination series with each other. The principal series of singlets of the normal atom is, as usual, $1S - mP$ where m has all values from 2 up, S equals 84178.5 and P equals 30112.8. When m is made 2 in this formula the first line of the series is

found to be 1849.6Å.—the limiting line ($m = \infty$) is 1S which has a wave-length 1188Å. This is the absorption series of the normal atom of which we have already spoken developed by electrons falling back from the exterior unstable orbits into which they have been thrown from the fundamental orbit. Fig. 6 shows the first four lines of this series. The check of Franck and



Einsporn's experimental results with those calculated from the series formula is seen to be excellent.

From the same fundamental orbit, 1S, a combination series of triplets is also developed as represented by the formula $1S - mp_{1, 2 \text{ or } 3}$ ($p_1 = 40138.3$, $p_2 = 44768.9$, $p_3 = 46536.2$ —the small letters referring to the triplet orbits, the large letters to the singlet orbits). Now although only the middle term, $1S - mp_2$, of each of these triplets is observed in emission and absorption by optical methods nevertheless an examination of the results of Franck and Einsporn shows a break at 4.68 volts and one at 5.47 volts corresponding exactly to radiation of 2656.5Å. and 2270.6Å., respectively, the two outside lines of the first triplet of this series. Since these outside lines are unknown in the optical spectra it has been concluded that electrons cannot ordinarily fall from these orbits to the fundamental orbit. In this connection we note

the break at 5.76 volts which indicates an inelastic impact supplying exactly the energy necessary to throw the electron from the $2p_3$ orbit entirely out of the atom, giving in two steps the total energy, 10.39 volts, necessary for ionization. To give opportunity for the two successive impacts on the same atom necessitated by this type of ionization we must suppose that the electron remains in the $2p_3$ orbit for a longer time than the usual 10^{-8} second given for displaced electrons to circulate in their outer orbits. An atom with an electron in one of these pseudostable exterior orbits from which it cannot readily return may be said to be in a "metastable" state. It is apparent that mercury in the $2p_3$ form of metastability can be ionized by applied voltages under 6 volts. This is an important conclusion having a bearing on the puzzling maintenance of arcs in mercury vapor at low voltages. The metastability may be brought about, of course, either by impact or by the absorption of radiation produced elsewhere in the arc.

This work of Franck and Einsporn is remarkably well suited to illustrate the points of this paper, but we cannot leave it without remarking that other observers have generally found only two resonance potentials for mercury— $\nu = 1S - 2p_2$ and $\nu = 1S - 2P$. When one has a long series of somewhat irregularly placed points on graph paper it is frequently possible to get partial curves intersecting almost anywhere. The results of less skilled experimenters who have followed in Franck and Einsporn's steps in recent months demand critical scrutiny.

Two other series, $1S - ms$ and $1S - md$, arise from the $1S$ orbit of mercury. An examination of the eighteen breaks in the curve of Fig. 4 now shows all of the lines terminating in the $1S$ orbit to be accounted for with a number left over. Whatever may be thought of the flexibility of the conclusions drawn from this particular research it cannot be denied that work of this kind has furnished valid evidence of the existence of energy absorptions corresponding to the occupation of successively enlarged stationary states by the electrons of stimulated atoms.

Although the mercury atom is, as has been said, an easy one with which to experiment, its structure is nevertheless complex. With an atomic number of 80 its shell construction, according to Bohr's latest theory,⁷ is (nucleus + 80) electron shells -2, -8, -18, -32, -18, -2. Its spectrum contains 177 lines. It must be

remembered, however, that all of these lines of the optical spectrum are developed by the two outermost electrons being to a large extent unaffected by the complex interior of the atom. The interior shells are, as is well known, involved in the production of X-ray spectra lines, the quanta of which are very large and the frequencies correspondingly high.

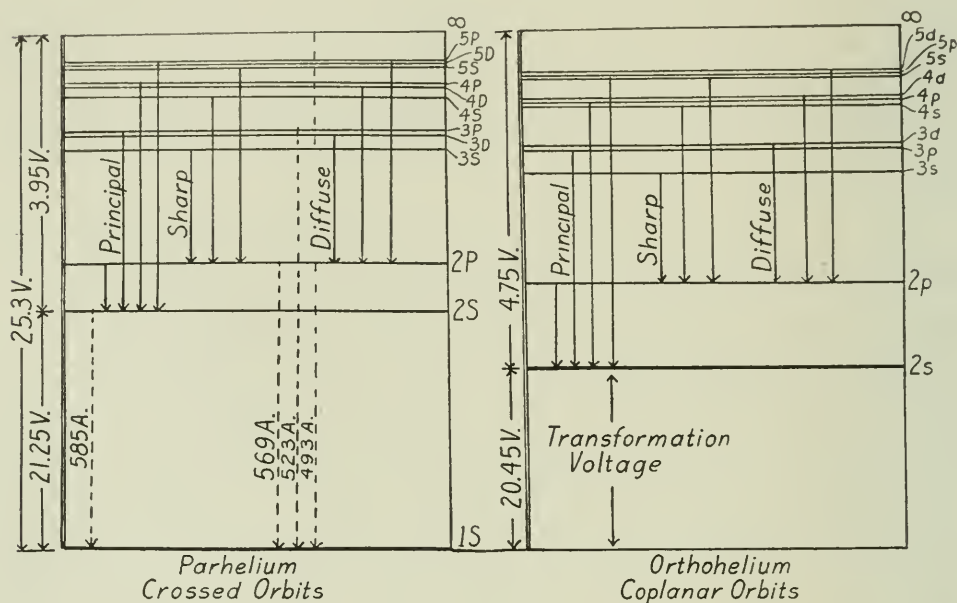
Let us now turn our attention to helium—that gas which of all others on account of the simplicity of its structure would seem to offer the most promise of successful investigation of its interior dynamics. Although hydrogen has a simpler atom than helium yet its tendency to form molecules renders it in experimental work less easy to deal with. The helium atom, being structurally simple, (nucleus + 2) electron shell —2, one might expect that its secrets would soon have been penetrated but, as a matter of fact, for many years it has furnished physicists with an interesting puzzle.

Bohr in his first representation of the helium atom supposed the two electrons to be diametrically opposite in the same orbit. On this basis he easily calculated that the energy necessary to remove one of the electrons to infinity, that is, to ionize the neutral atom, corresponded to that of a 28.8 volt impact. Franck and Hertz⁸ found a point of inelastic impact in helium at 20.5 volts which they interpreted as the ionization potential, but the presence of a third electrode in their device made it equally possible to ascribe the observed effect to a radiation potential—the photo-electric emission from the collecting electrode producing an effect indistinguishable from that due to plus ions developed in ionization. The first determination of the helium ionization point in a two-electrode device was made by Bazzoni⁹ in 1916. The result showed unmistakable ionization close to 20 volts. About the same time Richardson and Bazzoni showed by a photo-electric measurement that there is radiation in the helium arc of a wavelength which at the lowest value must correspond to impacts of about 26 volts energy indicating that true ionization cannot take place below that voltage. These facts, together with others collected in the same series of experiments, led Richardson and Bazzoni¹⁰ to formulate a theory, published in 1916, that impact ionization is not a simple phenomenon but that it is facilitated by radiation absorption so that ionization can result from impacts on atoms in an abnormal condition caused by the absorption of

radiation generated in other atoms in consequence of electron impact. The ionization potential might therefore be shifted back to the first resonance potential as its limiting value. This idea has been developed mathematically during the past year by K. T. Compton¹¹ and has been found adequate to explain the observed effects.

The spectrum of helium is very peculiar being divided cleanly into two independent sets of series, principal, sharp, diffuse, and so on, exactly as if the gas were made up of two different kinds

FIG. 7.



of atoms. This implication is so definite that formerly two kinds of helium were supposed to co-exist, orthohelium and parhelium, the first being distinguished by a spectrum of double lines, the second by a spectrum of single lines. The energy relations of these series are shown in Fig. 7.¹² The optical spectra, represented by the solid arrows in the figure, are seen to stop short of the innermost orbit. None of the lines so shown are absorption lines indicating that of the transitions represented, none terminate in the normal atomic configuration. The lines, consequently, whose frequency numbers would enable us directly to calculate the ionization potential do not appear in the ordinary optical spectra. They lie in the extreme ultra-violet and are being investigated at the present time by Lynian with his vacuum spectrograph. These ultra-violet lines corresponding to transitions

from and back to the fundamental $1S$ orbit constitute the absorption spectrum of helium. They are shown in Fig. 7 by dotted arrows. The results published by Lyman¹³ last summer do not fit in well with the numerical details about to be stated nor with the numbers given in Fig. 7. The explanation of these discrepancies will be pointed out later. The facts most generally accepted at the present time and represented in Fig. 7 are these—that the normal atom is the $1S$ state of parhelium, that in this atom, called the crossed-orbit atom, the two electrons revolve in very slightly elliptical orbits inclined at an angle of 120 degrees to each other; that orthohelium is a metastable form, the lowest possible energy state being the $2s$ orbit which can be reached from the normal state only by an energy absorption from impact or ultra-violet radiation corresponding to 20.45 volts. This is called “the transformation voltage.” In this metastable state the two electrons revolve in coplanar orbits one outside the other. For this reason orthohelium is frequently called “coplanar” helium. This $2s$ state, possessing as it does considerable stability, serves as the fundamental orbit for the optical series of orthohelium. An energy absorption of 21.25 volts by the normal atom will give us parhelium in the $2S$ state which also possesses some stability, though not as much as the $2s$ state, and is the fundamental orbit for the optical series of parhelium. The energy necessary to throw the electron into its $2s$ or $2S$ orbit, respectively 20.45 and 21.25 volts, plus that necessary to remove the electron from those orbits to infinity, respectively 4.75 and 3.95 volts, is taken to be the ionization energy of the normal atom. It will be seen that ionization is possible under this scheme with any electron bombardment energies greater than 20.45 volts but that true ionization by a single impact on a normal atom ought to require 25.3 volts.

It must be admitted that the experimental evidence for any notion as to the true fundamental orbit being the $1S$ state of parhelium is meagre and not too concordant but the results of Franck and Knipping,¹⁴ Franck and Reiche,¹⁵ Horton and Davies¹⁶ and Compton¹⁷ have united in establishing the existence of a resonance potential at 20.5 volts, of another resonance potential at 21.3 volts and of an ionization potential at 25.3 volts thus accounting for visible spectral lines as exemplified in the figure. Of these potentials the first, 20.5 volts, is the transformation voltage which ought not to cause any radiation since the

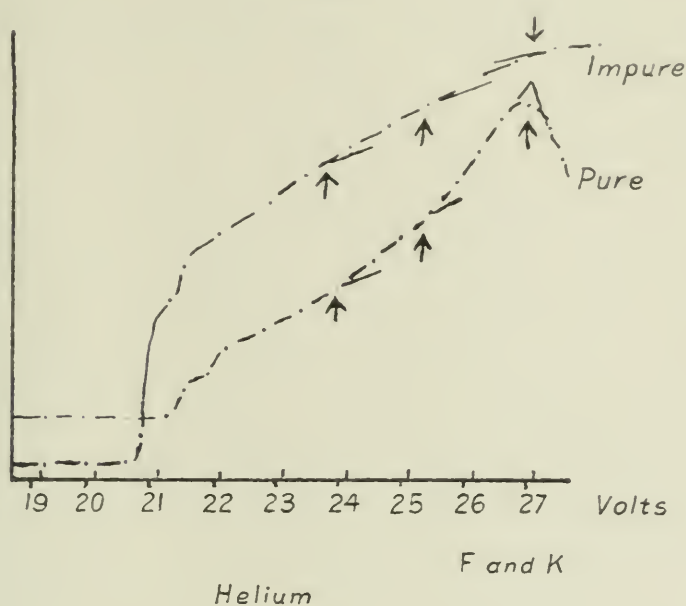
atom is thereby thrown into a metastable form from which it cannot return directly to the normal state. The second, 21.3 volts, corresponds to a radiation of wave-length 585\AA . and the third, the ionization potential 25.3 volts, to a radiation of wave-length 493\AA . which, therefore, ought to be the ultra-violet limit of the helium spectrum. Other less firmly established inelastic impact potentials have been observed at 21.9 volts (corresponding wave-length 569\AA ., $1S-2P$) and 23.6 volts (corresponding wave-length 523\AA ., $1S-3P$).

Lyman's results of last summer, referred to above, establish however by direct spectroscopic observation the presence of lines of wave-lengths 515.7\AA . (23.92 volts), 522.3\AA . (23.62 volts), 537.1\AA . (22.97 volts) 584.4\AA . (21.12 volts) and, less certainly, 600.5\AA . (20.55 volts). The calculated limit of this series is wave-length 502\AA . (giving 24.6 volts as the ionization potential). The publication of Lyman's results has led Franck¹⁸ to reëxamine Franck and Knipping's values and to correct their volt-meter readings by 0.7 volt thus giving an exact concordance between their impact values (suitably corrected) and Lyman's spectroscopic observation. A concordance so obtained is not very convincing and we can only conclude that the impact potentials of helium require further study. This need is the more apparent when we note that the only published calculation (Van Vleck's¹⁹) of the ionization potential of crossed-orbit helium gives 20.7 volts and not 24 or 25 volts as the observations above quoted would seem to demand.

Fig. 8 will serve as an example of some of the experimental results of the impact investigations. This figure gives the results of certain studies made by Franck and Knipping on the radiation developed from helium. The significant breaks which support the theory are indicated by arrows as otherwise they might be overlooked. There are, however, curves made by other methods which give more unmistakable break points. This figure is used in order to bring out the fact that in absolutely pure gas the 20.45 radiation corresponding to the breakdown of the metastable coplanar orthohelium is absent, indicating, apparently, that orthohelium once formed by impact can return to parhelium only in the presence of some impurity. This may be

explained by noting that $2S$ orthohelium is structurally like lithium, having a single electron in an exterior orbit, and ought, therefore, to possess a definite chemical reactivity. This means that in the presence of a molecule with which the atom might react, strong molecular electrical fields must be developed. It is the presence of these strong fields which renders possible the return of the coplanar atom formed by a 20.5 volt impact to the normal crossed-orbit form liberating the radiation shown by the rise in the curve in the diagram. In the absence of impur-

FIG. 8.



ity the extra electrical field is also absent and this return cannot take place; hence the absence of 20.5 volt radiation in the pure gas. That the interchange from the orthohelium to the parhelium form should be possible only in the strong field is rendered plausible by a mathematical development of the Bohr theory into which we cannot enter here.

It is interesting to note that the probable chemical activity of metastable helium may explain the progressive absorption of helium in the metal films inside vacuum tubes.

In summing up we may say that impact investigations have explained in a general way the optical series of helium and that unquestionably helium atoms possess above their fundamental orbits certain metastable states with different electron configura-

tions. We are not yet justified, however, in saying anything definite about the energy content or real arrangement of the fundamental orbit. The calculations which Bohr has promised to publish bearing on this matter will furnish fresh material for the experimentalists to work on.

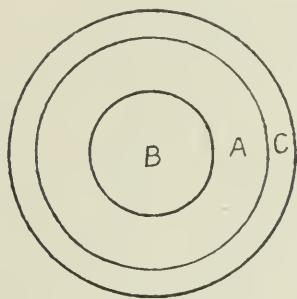
It is impossible within the limits of this paper to say anything about the interesting, if somewhat complicated, results which impact methods have given when applied to polyatomic molecules. In these cases the energies of dissociation must be considered in connection with the ionization and resonance energies. When this subject is fully worked out it may be expected to throw light on the mechanism of monomolecular chemical reactions.

We might mention in this connection the recent work of Franck and Cario²⁰ who found that atoms in a stimulated state, that is with electrons in exterior unstable or metastable orbits, can give up their excess energy merely on contact with unstimulated atoms or molecules. The particular observation was that such stimulated mercury atoms dissociate the hydrogen molecule into its atoms during the ordinary contacts which occur due to molecular agitation. This is neither impact transference nor radiation transference but is nevertheless a type of energy interchange which we might easily expect to occur.

It now remains to consider briefly the stimulation of spectral lines by the absorption of radiant energy. The atom can be stimulated to emit radiation whenever certain definite energy quantities are imparted to it exactly sufficient to lift some of its electrons into an exterior possible orbit. It does not matter how the energy is supplied. If the gas is subjected to radiation instead of to electron bombardment an emission will occur if the quantum $h\nu$ of the incident radiation has the critical magnitude necessary to lift an electron into an exterior orbit. This critical frequency, ν , is referred to as the resonance radiation of the atom. The absorbed radiation of frequency ν is reëmitted with the same frequency. This so-called resonance effect was demonstrated by Wood²¹ who showed that sodium light passed through sodium vapor was capable of stimulating the emission of the *D* lines. The most interesting and significant of recent researches in this field is by Fuchtbauer.²² Fuchtbauer made use of a quartz mercury lamp of novel construction. A cross-section of this

lamp is shown in Fig. 9. A discharge was maintained in the annular tube *A* by the usual methods. The space *B* contained cold mercury vapor. The chamber *C* was filled with liquid mercury and acted as a cylindrical reflector to concentrate the radiation from *A* into *B*. The radiations stimulated in the cold vapor in *B* were then photographed through a plate at the end of the device. The wall of *B* was of such thickness that the strong ultra-violet line, λ 1845, was thought to be entirely absorbed so that the bulk of the short radiation received in *B* must have come from the next strong line, λ 2537. The radiation stimulated in the cold vapor by this absorption of λ 2537 was found to consist of over thirty measurable lines. The probable way in which

FIG. 9.

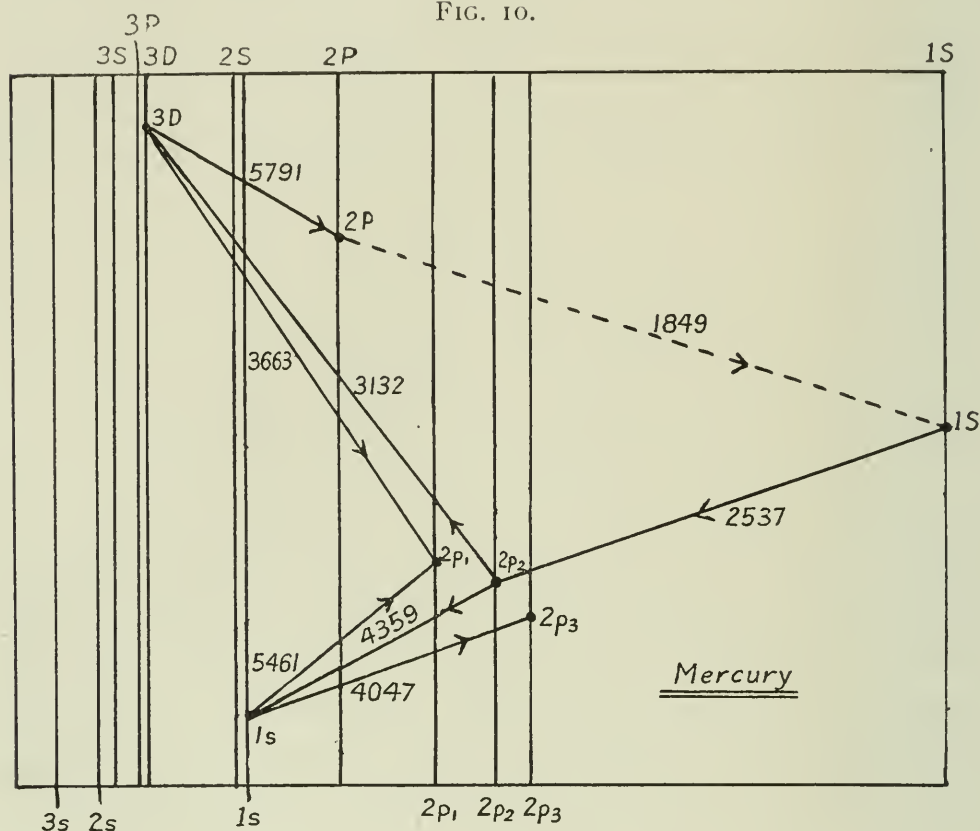


these radiations were developed is shown in Fig. 10. Here the spectral terms corresponding to the various energy levels are represented by dots, their relative magnitudes being proportional to their distances from the atom centre which lies to the right of the figure. Some of the possible transitions are shown in the figure by arrows, absorptions of energy corresponding to transitions to the left, emissions to transitions to the right. It will be noted that the primary absorption of λ 2537 throws the atom into the state where it may finally radiate λ 1845, a radiation which has a higher energy quantum than the original stimulating radiation. Study of this investigation throws much light on the complex interchanges which go on in arc discharges tending to alter in various ways the normal stability of the atomic systems. The facts thus brought out are of such significance that further study of them is desirable. It ought to be more definitely established that the stimulating light contains no wave-lengths shorter than λ 2537.

Conditions such as we have in Fuchtbauer's mercury column account for the persistence in arcs of atoms in stimulated states

for appreciable lengths of time (of the order of hundredths of a second) as observed by a number of experimenters. Again, whenever there is metastability there will be, by definition, a persistence of stimulated states over a certain time and therefore a persistence of the emission of radiation after the cessation of the original cause. The active nitrogen of the chemist, one of the principal characteristics of which is the ability to retain lumi-

FIG. 10.

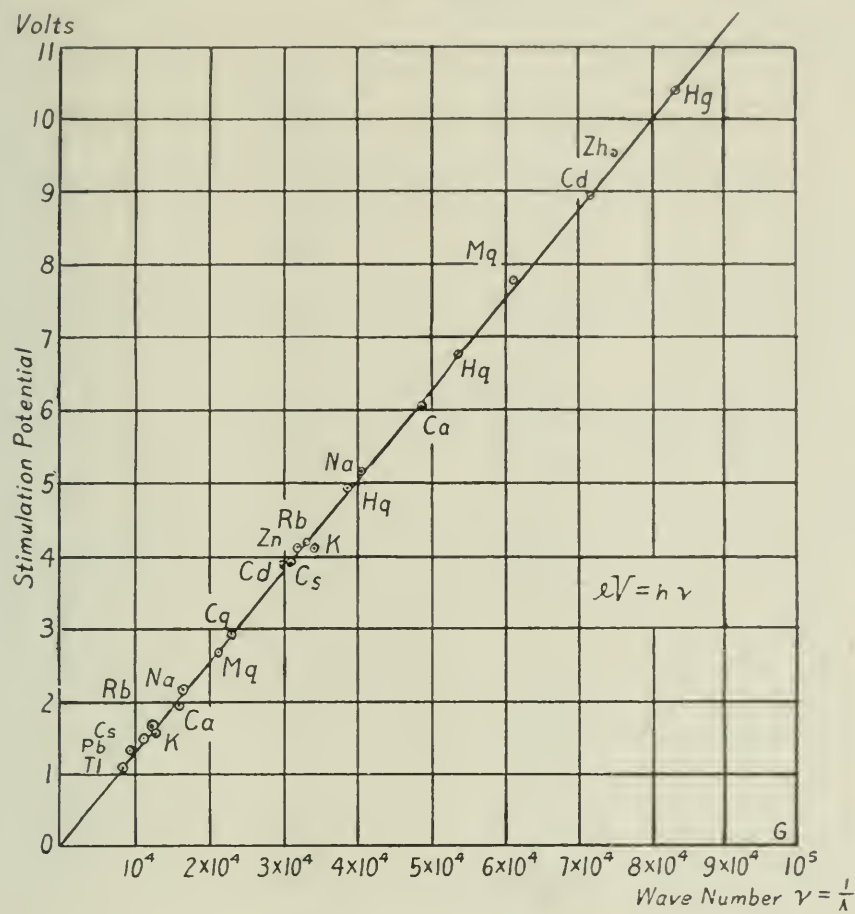


nescence after the cessation of a discharge passed through it, is thus seen to be possibly a metastable form of nitrogen. Swelled up atoms with occupied exterior orbits possessing as they do a less stability will in most cases possess a greater chemical reactivity than the normal forms.

In concluding this incomplete survey of ionization and resonance phenomena it will be useful to show that the measurements, which have now been carried into most of the columns of the periodic table, possess, on the whole, considerable precision. It is easily seen that when an ionization potential can be definitely associated with a corresponding spectroscopically observed line

the relation $eV = h\nu$, if plotted with the spectroscopic ν against the electrically measured energy eV necessary to stimulate it, will give a straight line the slope of which is Planck's constant h . Fig. 11 gives such a graph. An idea can be obtained from the figure, which is not complete to date, of the range over which the measurements have been extended. The data used in the graph

FIG. 11.



is tabulated in Fig. 12. The average value of the slope is seen to be 6.56×10^{-27} ergs seconds while the value for h at the present time accepted as best, determined by seven independent methods, is 6.554×10^{-27} . This agreement is sufficiently good to establish the methods of impact measurements among the more dependable of experimental physics. A large percentage of the values here tabulated were determined by Foote and Mohler and their associates²³ at the Bureau of Standards.

I have endeavored in this paper to show how Bohr's theory is related to the series formulas representing optical spectra and

to give a sufficient number of illustrations to make clear that experimental measurements have uniformly combined to prove the validity of the interrelation. I have endeavored, furthermore, to show that atoms and consequently molecules in a bath of

FIG. 12.

Periodic Group.	Element.	Potential in Volts. R — Radiation. I — Ionization.	Wave-length Å.	Series-term.	h
1	Na	2.12 R	5889.9	1S-2P	6.63
		5.13 I	5895.9 2912.6	1S	6.57
	K	1.55 R	7664.9	1S-2P	6.32
		4.1 I	7699.2 2856.7	1S	6.22
	Rb	1.6 R 4.16 I	7800.3 2968.4	1S-2P 1S	6.61 6.54
2	Cs	1.48 R 3.88 I	8521 3184.2	1S-2P 1S	6.69 6.58
	Mg	2.65 R	4571.4	1S-2p	6.43
		7.75 I	1621.7	1S	6.67
	Ca	1.9 R	6122.5	1S-2p	6.54
		2.85 R	4226.9	1S-2P	6.38
		6.01 I	2027	1S	6.45
	Zn	4.1 R	3075.9	1S-2p	6.70
		9.5 I	1319.9	1S	6.66
	Cd	3.88 R	3260.17	1S-2p	6.71
		8.92 I	1378.69	1S	6.53
3	Hg	4.9 R	2536.7	1S-2p	6.60
		6.73 R	1849	1S-2P	6.60
		10.35 I	1187.99	1S	6.53
4	Tl	1.07 R 7.3 I	11513	1S-2p	6.53
4	Pb	1.26 R 7.93 I	10291		6.87
Accepted "best" value from seven independent methods 6.554×10^{-27}			Average 6.56×10^{-27}		

radiation, however produced, are powerfully affected and frequently fundamentally altered in their dynamic constitution, being thrown into metastable forms in which their reactivities are often intensified or even changed in nature. Looking forward it

certainly seems that further advances in the fields here under discussion can be depended upon to furnish solutions for some of the basal problems of atomic and molecular interactions which have always underlaid the science of chemistry but which have heretofore eluded investigation.

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Action of Natural Waters on Lead. JOHN C. THRESH (*Analyst*, 1922, **47**, 459-468, 500-505) has studied the corrosive action of natural waters on metallic lead. Pure water has no action on lead; but action occurs in the presence of oxygen; plumbic oxide or hydroxide is then formed and remains in solution in a colloidal condition. Certain organic compounds, which occur in moorland waters, tend to retard the oxidation of the lead, but also tend to retain in solution any lead which is dissolved. The corrosion or oxidation is retarded by the presence of silicates, but not by the presence of sulphates, chlorides, carbonates, bicarbonates, or an excess of carbonic acid.

J. S. H.

The Electrical Structure of Matter. SIR ERNEST RUTHERFORD. (*Science*, Sept. 21, 1923.)—This is the presidential address before the British Association for the Advancement of Science at its meeting in September, 1923, at Liverpool. In these twelve pages is summed up with admirable clarity the present condition of our knowledge of the structure of the atom. It is to this article that he must turn who desires to inform himself of the state of affairs on this frontier of scientific investigation. Of much that he relates the eminent author might well have added "quorum pars magna fui," yet he keeps himself in the background.

To counteract some popular but too enthusiastic hopes, the following may be quoted: "It is well known that the total evolution of energy during the complete disintegration of one gram of radium is many millions of times greater than in the complete combustion of an equal weight of coal. . . . This possibility of obtaining new and cheap sources of energy for practical purposes was naturally an alluring prospect to the lay and scientific man alike. . . . With increase in our knowledge of atomic structure there has been a gradual change of our point of view on this important question, and there is by no means the same certainty to-day as a decade ago that the atoms of an element contain hidden stores of energy."

G. F. S.

Sodium Sulphate.—ROGER C. WELLS is the author of a monograph on "Sodium Sulphate: Its Sources and Uses" (*U. S. Geol. Survey Bull. No. 717*, 43 pp., 1923). This salt occurs in nature in the anhydrous condition as Thenhardite, as the decahydrate or Glauber's salt (mirabilite), and as a constituent of several complex minerals, chiefly double sulphates. In addition to the natural product, sodium sulphate also enters commerce as salt cake and niter cake which are by-products of the manufacture of hydrochloric acid and nitric acid, respectively. Niter cake also contains sodium acid sulphate and pyrosulphate. Natural deposits of sodium sulphate occur in at least eleven states west of the Mississippi River, in Canada, Mexico, and the Argentine, also in the eastern hemisphere. Sodium sulphate is used chiefly in the manufacture of wood pulp, glass, and sodium sulphide, to a lesser extent in dyeing, tanning, ore flotation, and medicine.

J. S. H.

Dakin Solution.—Dakin solution is a buffered aqueous solution of sodium hypobromite, and is used as a bactericide. When prepared from chloride of lime and a mixture of carbonate and bicarbonate of sodium, Dakin solution frequently has a pink color. J. HOLDEN (*U. S. Naval Med. Bull.*, 1923, 19, 156-157) states that this pink color is due to the presence of sodium permanganate; manganese may be present in the chloride of lime as calcium manganate, and is converted into sodium permanganate in the preparation of the Dakin solution. The presence of permanganate is believed to be desirable rather than objectionable.

J. S. H.

STUDIES IN PHOTOGRAPHIC SENSITIVITY.*

III.

TOPOCHEMISTRY OF DEVELOPMENT AND SENSITIZING NUCLEI.

BY

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Research Laboratory, Eastman Kodak Company.

THE term "topochemistry," in reference to the silver halide grains of photographic emulsions, embraces effects which can be related to the *position* of a component in the grain, and refers principally to distinctions between effects on the outside (surface) and the inside of the grain.

These distinctions were sufficient when the crystalline character and structure of the grain were less precisely known; at the present time, not only is the crystallographic structure accurately known,¹ but statistical data on the sizes, shapes, and orientations of the grains in emulsions are being rapidly obtained.² Consequently, a "topochemical" reference to a silver halide grain may well require much greater precision of statement. Surface distribution, for example, covers both edge and plane faces (on polyhedra) and does not differentiate between cubic and octahedral faces. But these finer distinctions will not be considered until necessary, and the term "topochemical" will be used in the broad sense unless otherwise specified. While many workers have at one time or another made use of "topochemical" considerations in dealing with the photographic emulsion, it is to Lüppo-Cramer that we owe the most numerous, as also the most varied and ingenious, applications of this conception.³

Although in certain cases, we may disagree more or less con-

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¹ A. P. H. Trivelli and S. E. Sheppard, "The Silver Bromide Grain of Photographic Emulsions," Eastman Kodak Company, Rochester, N. Y.

² Cf. E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard, *J. Phys. Chem.*, **27**, 1, 141, 466 (1923); *JOUR. FRANK. INST.*, **194**, 485 (1922).

³ As we shall have occasion to refer repeatedly to this author's publications on the subject, we shall leave references to their specific occasions.

siderably with Lüppo-Cramer's contentions, we should like to acknowledge the wealth of new facts which he has brought to light and the fertility of thought which he has applied to their explanation.

I. EFFECT OF IODIDE AND NUCLEUS EXPOSURE.

The introduction of iodide into the silver bromide grain has been shown to lead to a considerable number of distinct and remarkable effects.⁴ In explanation of effects produced by:

1. Presence of silver iodide in the emulsion.
2. Treatment of silver bromide emulsions previous to exposure, resulting in:
 - (a) Increase of "sensitivity" for physical development.
 - (b) Red sensitizing for chemical development.⁵
3. Treatment after exposure, prior to development, or incorporation in the developer, resulting in:
 - (a) Acceleration of development for certain developers (Lainer effect).
 - (b) "Fogging" with physical development.

Lüppo-Cramer has introduced and developed the hypothesis of "Keimblosslegung," which we shall refer to as "nucleus exposure."

At its simplest, the conception is that certain reagents interacting with silver halide grains may mechanically disintegrate them so that occluded silver nuclei are exposed, and become reactive. This conception was applied particularly to the various "iodide effects" instanced above. But in order to cover cases where the iodide is incorporated early in the emulsion, the hypothesis has to be modified. Lüppo-Cramer has pointed out, quite correctly, that its effect, *whatever the mechanism*, will itself depend upon its distribution in the grain. This can vary from a homogeneous solid solution to a purely superficial coating. In order to extend his hypothesis to cover cases where the early presence of iodide in the grain produces effects similar to those obtained by its subsequent introduction, Lüppo-Cramer has introduced an auxiliary hypothesis of a very general character. This is the hypothesis of "facilitation of formation of free silver nuclei [germs] in consequence of the presence of silver iodide."

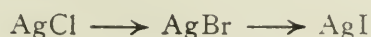
⁴ Cf. Lüppo-Cramer, "Kolloid Chemie u. Photographie," 2nd Ed.

⁵ F. F. Renwick, *Phot. J.*, 61, 12 (1921).

Although this was introduced as auxiliary to the earlier conception of mechanical "nucleus exposure," it appears that considerably different forces are involved, and that the ground is rather cut away under the mechanical concept. However, it is obvious that for effects produced when iodide is present in the emulsion—the mechanical disintegration hypothesis is not *sufficient*. Hence the query arises, is it *necessary* to explain the type (2) effects? Lüppo-Cramer's auxiliary hypothesis does not suggest a definite mechanism.

In a paper⁶ on the Lainer effect, the acceleration of development by iodide (on prebathing, or in the developer), one of the writers proposed a considerably different explanation. Namely, adsorption of reducing agents to the iodized grain, increasing the potential at the surface. In particular, this appeared more satisfactory in regard to the selective character of the Lainer effect, which is only shown with certain low potential developers.

This explanation does not seem entirely adequate in the case of the facilitation of "physical" development fog, and chemical "fog" (specific to certain developers and iodide concentrations) described in other papers.⁷ Here it was suggested that the silver iodide brought together both nascent silver and reducer. In the case of "physical" development⁸ we have moreover the known tendency of silver iodide to adsorb silver ions. This tendency increases along the series,



corresponding with the increased peptization and solution of the silver halides in solutions of silver salts.

If we may speak then of a general contact catalytic effect⁹ of silver iodide in photographic emulsions it appears reasonable that the adsorptive capacity of silver iodide must be borne in mind. This appears to have been neglected by Lüppo-Cramer in developing his general thesis of "facilitation, etc." Thus in his article on "The Characteristics of the Silver Iodide Image"¹⁰ he notes

⁶ S. E. Sheppard and G. Meyer, *J. Am. Chem. Soc.*, **42**, 689 (1920).

⁷ S. E. Sheppard, "Effect of Iodides, etc.," *Phot. J.*, **46**, 88 (1922).

⁸ Cf. Lottermoser, *J. prakt. Chem.*, **73**, 374 (1906).

⁹ Rather of a "promoter" than direct type.

¹⁰ *Phot. Korr.*, **50**, 561 (1913).

that a pure AgI emulsion—supposed free from reduction nuclei¹¹—when compared with a pure AgBr emulsion as similar as possible—gave on *physical development* before fixation somewhat higher sensitivity, and greater density. After fixation, the silver from the AgI emulsion was easily rubbed off. But if *physical development after fixation* was used, the AgBr emulsion showed the higher sensitivity (20° C. J. compared with 12° C. J.) and density. From this he concludes that the actual photochemical decomposition of the AgBr was greater, giving more nuclear material, but that AgI furnishes nuclei of greater activity in respect of the “typical grain surface development” operative in physical development.

In explanation of this he assumes that the nuclei are “obviously much more exposed in the first case, while in the silver bromide they are firmly enclosed and inactivated.” Hence he concludes that we cannot speak of a greater “light sensitivity of silver iodide, but only of a greater tendency to the formation of active nuclei for physical development.”

As against this, it would seem evident that the well-known high adsorption of *silver ions* to AgI affords an explanation of a considerable part of this result. The more rapid reduction at the surface would result in a less coherent deposit, as well as the higher apparent sensitivity. After removal of silver halide the situation would be changed—in fact, the residual silver nuclei might actually be more firmly occluded in the residual latent image after fixation. In any event, it will be observed that in the foregoing the function of the AgI is necessarily attributed to a *predisposing influence*, not to any actual mechanical disintegration.¹²

As further evidence of the adsorption factor, some results of A. Steigmann¹³ may be cited. In a paper on the reduction of sodium silver thiosulphate by sodium hyposulphite¹⁴ he states that the initial induction period, when no silver is precipitated,

¹¹ “Keimfrei.”

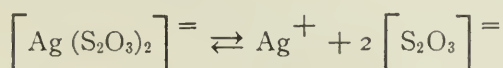
¹² In the case cited, Lüppo-Cramer finds that the nuclei on AgBr grains are more than on AgI after fixation. Yet elsewhere he states that when an AgBr plate is treated with KI before fixation, the opposite effect was observed, *i.e.*, more active nuclei after fixation than with plain AgBr.

¹³ *Koll. Zeits.*, **28**, 29 (1921).

¹⁴ NaHSO₂, often termed hydrosulphite.

may be overcome, by inoculating the solution either with colloid silver¹⁵ or with *silver iodide*. The catalytic effect of the latter Steigmann attributes to a relatively easier reducibility compared with the complex silver thiosulphate anion—although the latter furnishes silver freely once the induction period is passed! In his words, "In this case silver nuclei or nuclear complexes are formed from AgI before they can arise out of the difficultly reducible sodium silver thiosulphate in excess thiosulphate. Exactly the same results are obtained as on addition of (silver) nuclei in an inoculating solution. The nuclei formed from the AgI, which act as 'seed crystals' do not permit any supersaturation to occur in the further course of the reaction by which new nuclei could be formed."

First it seems contradictory to ascribe greater reducibility to the AgI than to the silver thiosulphate complex, when at the same time admitting that the latter can furnish a considerably supersaturated solution of metallic silver in the absence of colloid silver nuclei or silver iodide. We have a case of heterogeneous catalysis, in which the specific effect of the silver iodide is shown. In view of similar results in chemical reduction of silver bromide by one of the authors,¹⁶ a more probable explanation seems to be that here the AgI anchors to it both the reducer and the reducible silver anion. Further, an orientation of the complex silver anion could occur leading to a loosening of the silver, this favoring reduction. For AgI strongly adsorbs silver ions, and hence will favor displacement of the equilibrium



at its surface. Again, in any case, it is a predisposing influence of the AgI which must be called into account here, and not the "mechanical germ" exposure.

II. THE LAINER EFFECT.

In the cases just discussed, there can be no question of mechanical "Keimblosslegung." The Lainer effect consists in the acceleration of chemical development of AgBr by treatment

¹⁵ Cf. "Inoculation of Silver Sulphite Solutions in Excess Sulphite," S. E. Sheppard, *Phot. J.*, **59**, 136 (1919).

¹⁶ S. E. Sheppard, "Action of Iodides and Cyanides, etc.," *loc. cit.*

of the plate prior to development with dilute KI solution, or addition of this to the developer. It has been discussed fully by one of the authors elsewhere.¹⁷ The effect is limited to certain low potential developers, such as hydroquinone. As was pointed out in the paper referred to, it is a weak point of the mechanical explanation of this effect that it is thus selective.

Lüppo-Cramer has tried to obviate this by the idea that the "weak" developers which are catalyzed by KI are those which usually give only "grain surface" development, not penetrating the grain. But actually there is no evidence that hydroquinone does not give complete development of the grain, and a spongy silver grain. Further, with such a weak, or low, potential developer as ferrous oxalate, which is much more inclined to grain surface development, the Lainer effect is very slight or even absent."¹⁸ This was again tested on the "time of appearance," using a Chapman-Jones plate tester with a constant light source.

TABLE I.
Effect of KI on Time of Appearance of Image.
Seed Process Emulsion; Ferrous Oxalate Developer.

Expt.	Developer Concn.	Treatment.	Time in sec. Average of 2 expts.
1	N/10	H ₂ O	18
		N/10000 KI	11
		N/1000 KI	37
		N/100 KI	95
2	N/20	H ₂ O	45
		N/10000 KI	47
		N/1000 KI	75
		N/100 KI	157
3	N/10 Pure Bromide Emulsion	H ₂ O	23
		N/10000 KI	39
		N/1000 KI	49
		N/100 KI	110

Experiments (1) and (2) were made on Seed process emulsion, experiment (3) on pure bromide emulsion. It will be seen

¹⁷ S. E. Sheppard and G. Meyer, *loc. cit.*

¹⁸ Dr. Lüppo-Cramer has pointed out, since this was written (private communication) that von Hübl first obtained the Lainer effect with ferrous oxalate, and that he has also obtained it. It must be concluded then, from our negative results, that emulsion variations come in here (*cf.* S. E. Sheppard, *Phot. J.*, 46, 88 (1922)).

that, except in one instance, there is no acceleration but rather a retardation produced by pretreatment with potassium iodide. But with hydroquinone a very definite acceleration was produced :

TABLE II.
Effect of KI on Time of Appearance of Image.
Seed Process Emulsion; Hydroquinone Developer.

Expt.	Developer.	Treatment.	<i>t</i> in sec.
4	Hydroquinone 5.6 gms. }	H ₂ O	29
	Na ₂ SO ₃ 36 gms. }	N/10000 KI	14
	Na ₂ CO ₃ 75 gms. }	N/1000 KI	20
	H ₂ O 1000 c.c. }	N/100 KI	35
5	Ditto + the iodide*	H ₂ O	29
		N/10000 KI	28
		N/1000 KI	25
		N/100	15

* The difference when iodide is added to the developer had already been noticed (Sheppard and Meyer, *loc. cit.*).

With p-amidophenol, no acceleration was observed.

TABLE III.
Effect of KI on Time of Appearance of Image.
Seed Process Emulsion; p-amidophenol Developer.

Expt.	Developer.	Treatment.	<i>t</i> in sec.
6	P.A.P.	H ₂ O	12
		N/10000 KI	15
		N/1000 KI	21
		N/100 KI	45

While ferrous oxalate is very insensitive to potassium iodide, it shows marked acceleration in the presence of sodium sulphide, polysulphides, and sodium thiosulphate (*cf.* Table IV).

Yet these substances (sulphides and thiosulphate) have no such action with hydroquinone or other organic developers; further, their catalytic action with ferrous oxalate varies considerably from one emulsion to another. Taking these facts into consideration, the explanation of development catalysis by mechanical

nucleus exposure appears inadequate. The effects are too specific, and can be accounted for on other grounds.

III. NUCLEUS EXPOSURE AND OXIDIZING TREATMENTS.

If the Lainer effect and related effects do not necessitate "nucleus exposure" any more than the previously described influence of silver iodide in physical development, are there any cases in which it is a useful hypothesis? It is evident that if "nucleus exposure" facilitates reduction, by "freeing" the silver

TABLE IV.

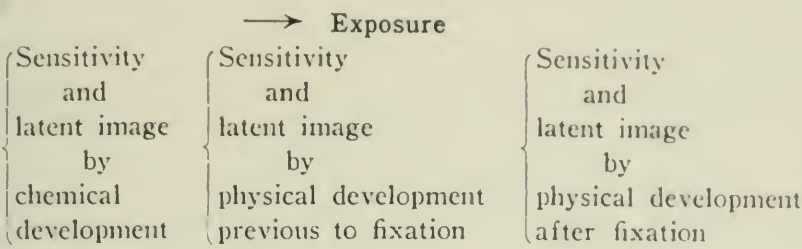
*Effect of Na_2S ; Polysulphides; and $\text{Na}_2\text{S}_2\text{O}$ on Appearance of Image.
Ferrous Oxalate Developer.*

Expt.	Plate.	Developer. Concn.	Treatment.	t in sec.
8	Pure bromide	N/10	{NaSH Bathed H_2O N/100000 N/10000 N/1000	21 28 10 Fog
9	Seed process	N/10	{NaSH Bathed H_2O N/100000 N/10000 N/1000	17 30 61 Fog
10	Seed process	N/10	{ $\text{Na}_2\text{S}_2\text{O}_3$ Bathed H_2O N/10000 N/1000 N/100	13 12 3 <3
11	Seed process	N/20	{ $\text{Na}_2\text{S}_2\text{O}_3$ In developer H_2O N/100000 N/10000 N/1000	40 37 34 16

nuclei, equally it should facilitate destruction of such nuclei by oxidizing agents. Experiments on this have been carried out both on the latent image and on the sensitivity.

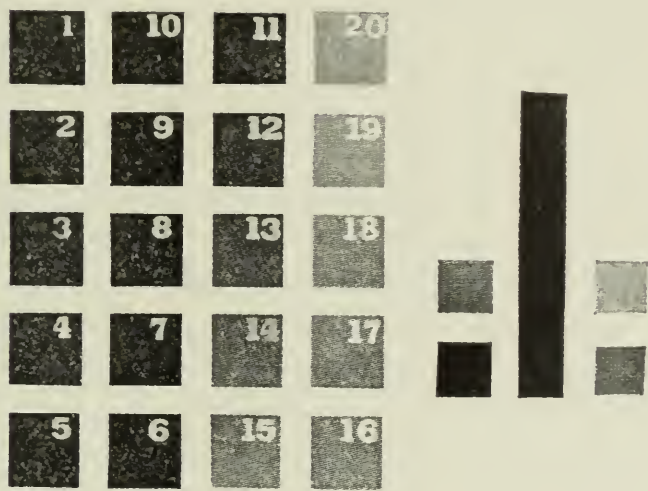
It should be noted that we must distinguish between at least three grades, or regions, of sensitivity and latent image, for any

given emulsion, according to the method of development. In terms of increasing exposure, we have broadly :



The experiments next to be described are of an orienting character, and only semi-quantitative. That is to say, instead of

FIG. 1.



The Chapman-Jones plate tester.

measurements of the characteristic curves, the extent of scale, or the “schwellen wert,” of a conventional plate tester was used. This was a Chapman-Jones plate tester¹⁹ (Fig. 1). Such testers have been invaluable in orienting, pioneer, and routine work, although not suitable for precision sensitometry.

Exposures were made to a 5-watt lamp, run off accumulators, and kept at a constant e.m.f. and amperage. The references to “degrees C. J.” will be clear from the figure.

¹⁹ Chapman-Jones, “Science and Practice of Photography,” London, 1904, p. 546.

IV. FOGGING ACTION OF POTASSIUM IODIDE BATHS.

Apart from the "red sensitizing" effect of iodide,²⁰ treatment of silver bromide plates with dilute KI solution leads to chemical fog, shown both for chemical and physical development.²¹ It is, however, much more marked in the case of physical development. According to the "nucleus exposure" hypothesis, the action is due to the disinterring of interior silver nuclei, large enough or active enough²² to initiate reduction in a developer. It is somewhat difficult to reconcile with this the greater tendency to production of "fog" by iodide for physical than for chemical development, since generally a considerably lower "nucleation threshold" is sufficient in the latter case.²³

If it be assumed that any silver iodide formed is less easily reduced on chemical development, why is this not operative for the same treatment in accelerating development with hydroquinone, etc.? A number of experiments were made, "spotting" plates of pure AgBr emulsion (no iodide) with dilute KI solutions. Further, both previous and subsequent treatments with chromic acid solutions were interpolated, with the object of destroying either original surface reduction centres, or such as might be exposed by the iodide. The results are given in Table V.

These experiments certainly do not give definite confirmation of the "nucleus exposure" hypothesis. In particular, the treatment with chromic acid *after* iodizing did not markedly reduce the fogging action of this, while treatment with chromic acid *prior* to iodizing did. This result is possibly due to the chromic acid treatment, in the second case, interfering with the iodizing by tanning the gelatin. In any case, the results seem more consistent with the adsorption hypothesis. The same results were obtained with a standard lantern emulsion. With this also the iodide fog on chemical development was much less than with physical

²⁰ S. E. Sheppard, "Action of Soluble Iodides, etc.," *Phot. J.*, **46**, 88 (1922).

²¹ *Ibid.*

²² Such ambiguity must be allowed in absence of precise knowledge.

²³ *Cf.* footnote (22). This corresponds to the greater light sensitivity of emulsions when chemical development is used.

TABLE V.

Fogging "Spot" Tests with KI on Pure AgBr Emulsion.

Expt. No.	Treatment.	Mode of Development.	Effect at			
			0	N/10000	N/1000	N/100
473	Spotted with KI solutions	Physical before fixation	None	Faint	Med.	Heavy
474	Spotted with KI. Then treated with .05 per cent. CrO_3 + .01 per cent. H_2SO_4 for five minutes. Rinsed and sulphated, washed.	Chemical Physical	None None	Faint Faint	Med. Med.	Med. Med.
475	Treated first with 5 per cent. CrO_3 , washed, etc., dried, then spotted with KI	Physical	None	Faint	Med.	Med.
478	Same, chromic acid, etc., as in 475	Chemical*	Faint	Med.	Med.	Med.
480	Spotted with KI, then treated with 1 per cent. CrO_3 + .25 per cent. H_2SO_4 , washed, etc.	Physical	Faint	Med.	Med.	Med.
481	Same as 480, but followed CrO_3 with sod. bisulphite	Physical	Faint	Faint	Med.	Med.
482	Treated first with 1 per cent. CrO_3 , washed, etc., then spotted with KI	Physical	None	None	Very faint	
483	Same, but used intermediate bath of bisulphite then KI	Physical	None	None	Very faint	

* Showed reversal at centre of spot.

development, and the effect of a chromic acid treatment was greater when used before than when used after iodide spotting.

V. POTASSIUM IODIDE TREATMENT AND THE REGENERATION OF LATENT IMAGE.

The extensive and valuable investigations of Renwick²⁴ have shown that the silver bromide of an exposed emulsion may be practically entirely converted to silver iodide with only slight loss of "latent image." Renwick's results have been confirmed and

²⁴ Hurter Memorial Lecture, *J. Soc. Chem. Ind.*, 39, 156T (1920).

elaborated by Lüppo-Cramer.²⁵ We shall not deal here with this reaction, but merely note that even strong potassium iodide solutions, provided the oxidation potential is kept down, have no marked destructive effect on the latent image. The effect we have to deal with now is one observed by Lüppo-Cramer²⁶ and affords, when positive, the strongest evidence yet adduced in favor of his original "nucleus exposure" hypothesis. As such, he has recently²⁷ introduced it in rebuttal of Sheppard and Meyer's criticism of his explanation of the Lainer effect. The new effect consists in the regeneration of latent image by treatment of an exposed plate with potassium iodide after it has been treated with chromic acid. It will be seen that the experiment is of the same type as that just discussed for fog. Lüppo-Cramer states that latent images on lantern plates were freed from the *soluble latent image*²⁸ by treatment with a chromic-sulphuric acid mixture; after thorough washing out of the chromic acid, which could be accelerated by pickling with concentrated Na_2SO_4 or KNO_3 solution,²⁹ one of the two plates thus treated was bathed one-half minute in a one per cent. KI solution, and then developed in the same physical developer as the other. The iodided plate showed after three minutes the whole Chapman-Jones scale, while the control gave nothing after thirty minutes. "Similar results were obtained with synthetic photobromide and photochloride."

²⁵ "Kolloidchem. u. Photographie," 2nd Ed.

²⁶ *Ibid.*

²⁷ *Koll. Zeit.*, 30, 186 (1922).

²⁸ Lüppo-Cramer considers, by this, that the latent image consists of a superficial portion, immediately active in ordinary developers, but easily removed by oxidizing agents, and an interior, more protected part. This latter can only function in catalyzing development when "exposed," or laid bare, and is similarly secured from destruction by oxidation, until "exposed." It forms the chief portion of the "latent image developable after fixation"—corresponding to Sterry's "organic latent image" (*Phot. J.*, 22, 264 (1898)). This view, which is consistent with many, though not all, of the reactions of the latent image, is not always maintained in this definite form by Lüppo-Cramer. Thus while at one time he refers to the solution of the superficial latent image by chromic acid, at another (*vide infra*, p. 670) he supports Sterry's view that the effect of chromic acid is only to delay development (chemical) not to destroy the latent image.

²⁹ *Cf. Phot. Ind.*, 1912, p. 572. Similar to the use of brine in the leather industry to pickle hides after souring.

In Table VI are given orienting results on the effect of chromic acid at different concentrations on (a) the latent image, (b) the sensitivity. These terms are used here formally, to signify that in case (a) the chromic acid, etc., treatment was used *after* exposure, before development, and in (b) *before* exposure. In saying provisionally that the effect in case (a) exhibits the destruction of "latent image," this shall not be interpreted as meaning complete

TABLE VI.
Action of Chromic Acid on Latent Image (a) and Sensitivity (b).

Treatment (5 minutes).	After- treatment.	S.*	Degrees Chapman-Jones.											
			Seed Graflex.		Seed Lantern.		Seed Process.		News Bromide		Contrast Velox.		Lippmann (washed).	
			173,000	5400	5400	1320	6	1						
Blank.	Blank.		25	25	25	25	25	23						
			a	b	a	b	a	b	a	b	a	b		
CrO ₃ 5% } H ₂ SO ₄ 1% }	NaHSO ₃ 5%	0	0											
CrO ₃ 2% } H ₂ SO ₄ 5% }	NaHSO ₃ 5%	0	19	0	14	0	15	0	15	18	25	0	25	
CrO ₃ 1% } H ₂ SO ₄ .25% }	NaHSO ₃ 5%	14	20											
CrO ₃ .5% } H ₂ SO ₄ .125% }	NaHSO ₃ 5%	15	22	0	17	0	18	15	17	20	25	0	25	
CrO ₃ .25% } H ₂ SO ₄ .06% }	NaHSO ₃ 5%	16	23	0	20	0	18	19	19	21	25	0	25	
Development			P.A.P. 4 mins.	P.A.P. 4 mins.	P.A.P. 4 mins.	P.A.P. 4 mins.	Nepera 1:4 4 mins.	P.A.P. 15 mins.						

* S refers to relative sensitivity, in terms of Lippmann emulsion as 1.

destruction, nor even as excluding paralysis of developability. Effectively, so much latent image is put out of action for a given type of development. Similarly, in case (b) any apparent or effective desensitizing may be due either to actual reduction of sensitivity prior to exposure, or to something remaining after the treatment, which destroys, or inhibits, the nascent "latent image." ³⁰ This latter possibility is largely discounted in the

³⁰ Cf. Sheppard and Mees, "Theory of the Photographic Process," p. 197.
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present case, because the after-treatment with bisulphite destroys any chromic acid, converting it to chromium sulphate³¹ which, although it tans the gelatin, does not affect either sensitivity or appreciably inhibit development. This was determined by separate and special tests, some of which will be described now.

VI. THE RETENTION OF CHROMIC ACID AND CHROMIUM SALTS BY GELATINO-SILVER BROMIDE EMULSION.

1. *Adsorption of CrO₃ to Precipitated AgBr.*

It has been previously suggested by one of the authors and C. E. K. Mees³² that chromic acid is appreciably adsorbed to silver bromide. This possibility has now been tested, using pure silver bromide precipitated in the dark in absence of gelatin. The AgBr was prepared by mixing equal volumes of:

(A) Solution of KBr 20.6 gms. in 250 c.c.

(B) Solution of AgNO₃ 29.4 gms. in 250 c.c.

Using 25 c.c. each of A and B, 5.0 gms. AgBr are formed. This was precipitated in red light, washed by decantation, and treated for twenty-four hours with chromic acid solution. The chromic acid in the solution was determined by the method of Fresenius and Cohn³³ with ferrous sulphate and permanganate. The results are given in Table VII.

TABLE VII.

The Adsorption of CrO₃ by AgBr.

Concentration of CrO ₃ .	Gms. CrO ₃ absorbed per 5 gms. AgBr.
.50 per cent.000
1.00 per cent.	— .001
2.00 per cent.	— .00036
3.00 per cent.	+ .00036
4.00 per cent.	+ .0003
5.00 per cent.	+ .0005

The adsorption, measured by the effective change in concentration, is less than the error of the method; it appears in any

³¹ Actually a complex chromium sulphate.

³² "Theory of Photographic Process," *loc. cit.*

³³ Fresenius and Cohn, vol. i, p. 424, New York, 1912.

case to be less than 0.0001 g. per 1 gm. AgBr. Control experiments on washing out chromic acid from the precipitate showed this to be washed out quantitatively according to the usual law, no appreciable quantity of chromic acid being left. Hence, it is concluded *that there is no appreciable adsorption of chromic acid to pure AgBr in absence of gelatin.*

2. Retention of CrO_3 by Gelatin.

The problem of the complete removal, or at least neutralization, of desensitizing and image destroying substances, prior to the operations of exposure and development, respectively, has seldom received sufficient attention. Yet where "topochemical" inferences are drawn from the results of a series of reactions carried out on the plate, for them to be convincing, proof is necessary that the earlier reagents have been removed. It is well known that the complete removal of certain substances from gelatin is a very difficult matter. As regards chromic acid, recent investigations³⁴ suggest that while this will combine with gelatin at H-ion concentrations less than $p_H = 4.7$, above this it should be uncombined and readily washed out.

We have found that careful neutralization of the chromic acid in the emulsion by treatment with solutions of Na_2CO_3 and NaHCO_3 is much more effective than either repeated washing alone or the "pickling" process of Lüppo-Cramer.

As illustrating the retention of chromic acid after repeated washing, 150 sq. cms. of Seed graflex plate were soaked two hours in a solution of .25 per cent. CrO_3 , .06 per cent. H_2SO_4 , and then washed in ten changes of distilled water, ten minutes each. The emulsion was then stripped, ignited, the reduced chromium oxidized to CrO_4'' with chlorine, and determined. Found .0235 gm. CrO_3 per 150 sq. cms.

When 5 per cent. NaHCO_3 was used for ten minutes, and only four washes in distilled water, only .002 gm. CrO_3 were found. If instead of Na_2CO_3 or NaHCO_3 , sulphites, as Na_2SO_3 or NaHSO_3 , are employed, chromic acid is reduced to the chromic condition (in part probably as complex anion). This has no

³⁴ Cf. J. Loeb, "Proteins," New York, 1922.

appreciable oxidation-potential as regards either the "sensitivity" or the "latent image."³⁵

But in order to be sure of this, it appeared desirable to be able to remove the chromium, which is now tenaciously retained by the gelatin, forming a chrome tanning. To effect this, advantage was taken of the action of polyhydroxy organic acids in dissolving chrome oxide and effecting detanning.³⁶ In the case of chrome-hardened gelatin, the solutions must not be too concentrated nor the temperature too high, or the gelatin becomes peptized. The following results were obtained with the same emulsion hardened for two hours in 1.25 per cent. chrome alum solution.

TABLE VIII.
Removal of CrO₃ from Plates.

No.	After-treatment.	M. P. °C.	Gms. Cr per 100 sq. cms.	Gms. Cr per gram dry emulsion.
0	(Blank)	37° - 38°		
1	Rinsed only	> 100°	.0055	.0143
2	3 washes 15 mins. in 3 per cent. citric acid	60° C.	.0011	.00287
3	3 washes 1 hr. in 3 per cent. citric ...	55° C.	.0008	.00205
4	3 washes 1 hr. then 15 hrs. in 3 per cent. citric	45° C.	.0003	.00082
5	3 washes 1 hr. then 15 hrs. in 5 per cent. citric	38° C.	.00008	.00020

It is concluded that a preliminary treatment with 3 per cent. citric acid, followed by 15 to 18 hours in 5 per cent. acid, kept at or below 60° F., removes all but traces of Cr. At the same time, the process is tedious, and generally unnecessary. It served to show that Cr retained by the gelatin had no pronounced inhibiting effect either upon exposure (sensitivity) or upon development (latent image).

3. Possible Effects of CrO₃ on the AgBr Emulsion and the Treatment Used Practically for Removal of CrO₃.

The question of removal or destruction is of critical importance. When a plate is treated (*A*) before exposure, (*B*) after

³⁵ Regarding "sensitivity" as partly determined, at least, by a precursor of the latent image other than silver halide.

³⁶ H. R. Procter and J. A. Wilson, *J. Soc. Chem. Ind.*, **35**, 156 (1916).

exposure, before development, the effects observed might be due to the following conditions:

<i>A</i>	<i>B</i>
Before Exposure.	After Exposure, Before Development.
(a) The oxidizer may destroy sensitizing nuclei. These may be colloid silver, or traces of substances in gelatin.	The oxidizer may destroy the latent image.
(b) ³⁷ The oxidizer, remaining in the emulsion, may destroy the nascent latent image.	The oxidizer may inhibit the development, <i>e.g.</i> , <i>poison</i> the development centres.
(c) The oxidizer, remaining in the emulsion during and after exposure, may interact with the developer and reduce its concentration.	

Of these, case (c) was applied by Sheppard and Mees to explain part of Sterry's results³⁸ with chromic acid. It was not suggested that all the phenomena were accounted for, since either an apparent destruction, or at least inhibition, of the latent image was observed, depending considerably upon the time of action and the concentration of chromic acid. This part of the action was unaffected by treatment of the chromated plates with neutral sodium sulphite previous to development.³⁹

Neutral sodium sulphite (Na_2SO_3) can have an independent action on the silver halide grain. This consists in partial solution and formation of a soluble complex silver salt, perhaps more readily reducible. It is in any case desirable to reduce this tendency, as well as the tendency to reduction, and for these reasons the bisulphite is preferable. It also produces a tanning complex with the chromic acid, which can be removed with citric acid if necessary.

In most cases, for relatively short treatment with not too concentrated CrO_3 —up to 2 per cent.—we find that a bath of 5 per cent. NaHCO_3 , followed by good washing, is sufficient to remove the CrO_3 . For "one-grain layers," subsequently noted, this treat-

³⁷ This theory of desensitizing (Sheppard and Mees, "Theory of Photographic Process," p. 261) has been adopted by Lüppo-Cramer for his safranin desensitizing process.

³⁸ *Phot. J.*, 54, 50 (1904).

³⁹ Sheppard and Mees, *loc. cit.* Cf. also Lüppo-Cramer, *Phot. Korr.*, 1909, p. 496. This author refers here to the use of sulphite for eliminating chromic acid, but misses the point since he overlooks the fact that Sheppard and Mees differentiated between the transient and the permanent effects of chromic acid.

ment is entirely adequate, but for ordinary emulsions the removal of CrO_3 must be tested.

VII. DESTRUCTION OF SENSITIVITY, AND REGENERATION.

Returning now to consideration of the results in Table VI, it will be seen that, generally, as the speed and the grain-size decrease, the "sensitivity" appears to be relatively less affected than the "latent image." The explanation of this does not appear to be in an actually greater resistance of the "sensitivity" in the finer grains. It is due to a sensitizing action of the bisulphite, which can be shown to have an actual independent sensitizing action on emulsions such as Lippmann, and even Seed process. Consequently, the Velox and the Lippmann emulsions do not show any desensitizing effect with this treatment, although in the latter case the "latent image" was wholly obliterated.

The bisulphite cannot regenerate "latent image" (which is differentiated or has gradation) and does not produce the analogue at this stage (after exposure), *viz.*, general chemical fog, to any great extent. Owing to this resensitizing effect, the results recorded here are of more importance for the "latent image," for which a considerable measure of destruction appears to be effected.

It has been asserted by Sterry⁴⁰ and by Vidal⁴¹ that the apparent destruction of the latent image by chromic acid is mainly a matter of retardation of development. Lüppo-Cramer's differentiation of the "latent image" into superficial, more soluble, and occluded, strongly adsorbed, less soluble portions has helped to clarify the issue here, particularly in regard to the residual "latent image" physically developable after fixation.

But Lüppo-Cramer has also stated⁴² that "furthermore the image appears almost unchanged, if ordinary development is only very greatly prolonged." This did not agree with results previously obtained by one of us (S. E. Sheppard) and was retested. It appeared more probable with fine-grained plates, which would be relatively more susceptible of a certain amount of secondary development, *i.e.*, combined fixation, by sodium sulphite, and physical development.

⁴⁰ *Phot. J.*, *loc. cit.*

⁴¹ *Photo. Archiv.*, 1895, p. 344.

⁴² *Phot. Korr.*, 1909, p. 495-496.

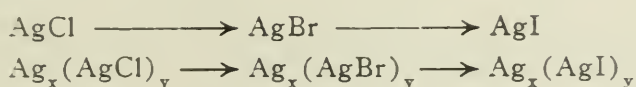
Seed lantern plates were treated with 2 per cent. CrO_3 , which was found to apparently destroy the latent image for ordinary development. An after-bath of 5 per cent. NaHSO_3 was used to destroy the residual CrO_3 . Development was effected with a solution of

7 grams p-aminophenol hydrochloride
50 grams Na_2CO_3
50 grams Na_2SO_3
1000 c.c. with water

This contains sufficient sulphite (5 per cent.) to exercise the "nucleus exposing" action asserted by Lüppo-Cramer,⁴³ or the possibly equivalent "secondary development" referred to above.

It was found that neither prolongation of the development for many hours, nor frequent renewal produced any trace of image. Yet when the same CrO_3 solution was used prior to exposure, and followed by bisulphite, about 17 to 18° C. J. were immediately and normally developed, as compared with 25° with no CrO_3 treatment. Tests on other plates gave the same result, so that we are unable to confirm the idea of mere retardation of development. It appears that chromic acid, at sufficient concentration, destroys most of the latent image active in normal chemical development.

Returning to Table VI, it will be noted that the latent image on N-bromide and on Velox shows considerably greater resistance than on the plates (Process, etc.) of coarser grain. This is due to difference of chemical composition. The Velox emulsion is practically entirely silver chloride, while the N-bromide contained considerable chloride as well as bromide. This result then is quite in agreement with Lüppo-Cramer's general conclusion that in the series



the photohalide stability *decreases* from the chloride to the iodide, or, in other words, the adsorption of colloid silver is strongest in the chloride.

⁴³ *Phot. Korr.*, 1912, p. 313. "Further experiments showed that the simple sulphite solution alone had a nearly equal effect [to that of 10 per cent. potassium ferrocyanide plus 5 per cent. sulphite] on the latent image treated with chromic acid."

TABLE IX.

*Action of CrO₃ and KI on Latent Image.
Graflex Plate; Exposed 20 sec. to Standard Light.
Developed 4 min.*

Expt.	Treatment.				Result in Degrees C. J.	
	1	2	3	4	Phys. Develop.	Chem. Develop.
487	Nil-Dry Plate				16	
527	Nil-Dry Plate				14	
528	Nil-Dry Plate				16	
491	Nil-Dry Plate					25
529	Washed, H ₂ O				19	
530	Washed, H ₂ O				20	
488	{ 1% KI	Washed, H ₂ O }			22	
492	{ 5% Na ₂ SO ₃ 1.5 min.					23
489	{ 1% KI	0.05% CrO ₃	5% NaNO ₂	Washed	15	
493	{ 1.5 min. Washed	0.01% H ₂ SO ₄ 5 min.	5 min.	}		24
490	{ 1% KI	0.05% CrO ₃	5% Na ₂ SO ₃	Washed	21	
517	{ 5% Na ₂ SO ₃	0.01% H ₂ SO ₄	5 min.	}	19	
494	{ 1.5 min.	5 min.				22
519	{ Washed					22
507	{ 1% KI	0.05% CrO ₃	Washed		22	
	{ 5% Na ₂ SO ₃	0.02% H ₂ SO ₄				
	{ 1.5 min.	5 min.				
	{ Washed					
508	{ 0.05% CrO ₃	12% Na ₂ SO ₄	Washed		15	
518	{ 0.01% H ₂ SO ₄				12	
525	{ 5 min.				13	
526					19	
505						25
520						25
503	{ 0.05% CrO ₃	12% Na ₂ SO ₄	1% KI	Washed		23
506	{ 0.01% H ₂ SO ₄	Pickled and washed	5% Na ₂ SO ₃	}	24	
	{ 5 min.		1.5 min.			
509	{ 1% KI	0.2% CrO ₃	Washed			15
	{ 5% Na ₂ SO ₃	0.04% H ₂ SO ₄				
	{ 1.5 min.	10 min.				
510	{ 0.2% CrO ₃	1% KI	Washed			15
	{ 0.04% H ₂ SO ₄	5% Na ₂ SO ₃				
	{ 10 min.	1.5 min.				

TABLE IX (cont.).

Action of CrO₃ and KI on Latent Image.
Graflex Plate; Exposed 20 sec. to Standard Light.
Developed 4 min.

Expt.	Treatment.				Result in Degrees C. J.	
	1	2	3	4	Phys. Develop.	Chem. Develop.
511	Same	1% KI No sulphite	Washed			15
512	Same	No KI	Washed			19
513	{ 1% KI 1.5 min.	{ 0.2% CrO ₃ 0.05% H ₂ SO ₄ 10 min.	{ 5% Na ₂ SO ₃ 10 min.	Washed }	13	
514	{ 0.2% CrO ₃ 0.05% H ₂ SO ₄ 10 min.	12% Na ₂ SO ₄	1% KI	Washed }	20	
515	{ 1% KI 1.5 min.	{ 0.2% CrO ₃ 0.05% H ₂ SO ₄ 10 min.	Washed }		0	
516	{ 0.2% CrO ₃ 0.05% H ₂ SO ₄ 10 min.	Washed }			0	
521	{ 0.2% CrO ₃ 0.04% H ₂ SO ₄ 10 min.	{ 12% Na ₂ SO ₄ Washed	{ 1% KI 5% Na ₂ SO ₃ Wash	Repeat 1, 2, and 3, then wash }	14 wet	
522	{ 0.1% KI 5% Na ₂ SO ₃ 1.5 min.	{ 0.2% CrO ₃ 0.04% H ₂ SO ₄ washed	12% Na ₂ SO ₄	Repeat KI then Wash }	15 wet	
520 523 524	{ 0.2% CrO ₃ 10 min.	{ Developed 8 min. instead of 4 min. 12% Na ₂ SO ₄ 10 min.	{ Washed Washed 0.5% KI 5% Na ₂ SO ₃ 1.5 min.	Washed }		19 19 20

(To be concluded.)

The Auroral Spectrum and the Upper Strata of the Atmosphere. L. VEGARD. (*Phil. Mag.*, July, 1923.)—In Professor Vegard's expedition to Bossekop in Finmarken during the winter of 1912-13 he photographed some of the blue lines in the

auroral spectrum. These were shown to belong to the negative band spectrum of nitrogen. In the winter of 1921 he continued his investigations at Christiania, where he is professor of physics, and measured the wave-length of the characteristic green line in the spectrum of the aurora. This equalled 5578.0 international units. Its origin, however, remained unknown. Last winter, 1922-23, three spectrographs at the Geophysical Institute, Tromsø, were used by him in further examination of the aurora. With an exposure of 15-20 hours the quartz spectrograph furnished a photograph of 21 lines. Thirty-five lines in all were measured, of which 29 belong to nitrogen and two are most likely bands of the same gas. There remain four lines of unidentified origin, of which one is the green line. "I think," he says, "there is little doubt that these lines also are due to nitrogen. This only means that the auroral spectrum is formed under conditions which are very difficult to reproduce in the laboratory." He emphasizes that "no indication of either hydrogen or helium lines has been observed." He has studied the light produced when cathode rays bombard a mixture of nitrogen and hydrogen on the one hand, and of nitrogen and helium on the other, and draws the conclusion, "The absence of H and He lines in the auroral spectrum, therefore, shows that in that region where the auroral light is emitted, the pressure of H and He must be small compared with that of N in the same region." This deduction is recognized to be contradictory to the results drawn from the assumptions of Wegener and also to the existence of a temperature of 300° absolute in the upper parts of the atmosphere derived by Lindemann and Dobson from a study of meteors. According to both of these other methods there should be a predominance of helium and hydrogen over nitrogen at a height of about 140 km. above the surface of the earth. This is in addition negated by the consideration that there should be a change in color of the auroral rays as they pass from heights of 300 km. down to 110 km. above the earth, were there such a notable change in the composition of the atmosphere along their path.

"I have found by spectral observations that the green line is seen to the very top of the auroral ray streamers, and the gas which emits this line must be a prominent component of the atmosphere up to its extreme upper limits. Hence we conclude that the hydrogen and helium layer, which has earlier been supposed to dominate at the top of our atmosphere, does not exist." He rejects the possibility of the origin of the line being due to a hypothetical element geocoronium. "The introduction of geocoronium is merely an easy way of getting out of the difficulty."

As a solution of some of the problems of the aurora the author suggests that the radiation of very short wave-length from the sun may drive negatively charged electrons from the nitrogen of the higher regions in the atmosphere. Thus there is left surrounding the earth a shell of positively charged nitrogen and by this the famous green line may be emitted.

G. F. S.

CORRESPONDENCE.

University of London, University College.

Gower Street, London, W. C. 1.

20th September, 1923.

Dear Sir,

I venture to send you the enclosed note for publication in your JOURNAL if it meets with your approval. It contains a short answer to R. W. G. Wyckoff, who in previous issues of your JOURNAL has criticized our work on the X-ray analysis of crystals.

Yours faithfully,

(Signed) W. H. BRAGG.

The Editor, of the

JOURNAL OF THE FRANKLIN INSTITUTE,

Philadelphia.

R. W. G. Wyckoff, discussing recently the relation between the X-ray analysis of crystalline structure and the conclusions of mathematical crystallography, has made statements (JOURNAL OF THE FRANKLIN INSTITUTE, Feb., March and April, 1923) which demand a reply. He condemns *in toto* all attempts at analysis which, as he puts it, have paid insufficient attention to the theory of space groups.

The theory of space groups is the final effort of geometrical crystallography: "The geometrical theory is now complete" (Hilton, "Mathematical Crystallography," p. 256). Having proved that there are 32 classes of crystal in regard to symmetry, as defined by the possession of different combinations of centre axes and planes of symmetry, it proceeds to show that in each class the possession of a particular combination is compatible with various relative positions of the axes and planes in space. The existence of a plane of symmetry may be due to the fact that the atoms and molecules of the crystal become self-coincident after direct reflection across the plane; or they may become so only after a shift in some direction or another; the same alternative is found in the case of an axis. In the cubic system, the axes of trigonal symmetry, which are necessarily present, may or may not intersect. Within each class, therefore, are variations of the actual movements which can bring the crystal to self-coincidence. Each such set of movements constitutes a "space group of movements." In all, there are 230 such sets, distributed among the 32 classes.

Now we may state this classification in another way. A crystal may be looked on as an aggregation of sets of atoms, which we may

call molecules since they are generally identical with chemical molecules. Given a certain number of molecules with which to form the unit pattern, it is possible to arrange them so that the unit and the crystal have certain degrees of symmetry, in other words, so that the crystal belongs to some one of the 32 classes. But, given the number and the class, there are in general several ways of arranging the molecules so as to obtain the symmetries of the class. Each of these ways corresponds to one of the 230 space groups, and each of the 230 can, therefore, be described in two ways. Given the necessary data as to the positions of the molecules, *i.e.*, as to the absence or presence of shifts, the various movements can readily be deduced, and *vice versa*.

If a crystal is examined by the older methods which depend on observations of form, its class can nearly always be determined, but not its space group. On the other hand, the X-ray methods can do all that the older methods could do except that they cannot detect the existence of a centre of symmetry and can also determine, in a great number of cases, those data regarding the relative positions of the molecules by which its space group is defined. This being done, the system may be denoted by the name or symbol which mathematical crystallography has given it. But no help towards the determination of structure is to be obtained in this way, because nothing has been, or can be, discovered about any space group except the possibility of its existence. The point up to which the study of symmetry can be of assistance has already been passed. Up to that point, the conclusions of mathematical crystallography can be most helpful in saving time and labor, though they can only prove the possibility of what the X-rays actually find. Beyond that point new ground is entered.

It is unreasonable, therefore, to reject results because they have been obtained without the use of the terms of the theory of space groups, since the terms which are more naturally used in the X-ray analysis are equally effective in expressing the laws of symmetry.

Let us take an instance. Suppose we are examining by the X-rays a crystal which has been shown by the older methods to belong to Class 7, the rhombic hemimorphic class: Such a crystal is resorcinol. The results of X-ray analysis show that the crystal unit cell is orthorhombic and contains four molecules, and they determine the dimensions of the cell. We now take into account the known polarity of the crystal and then conclude that the molecule has no symmetry: Since the crystal would belong to a class of higher symmetry if its four molecules had symmetry of their own. We might even be justified in assuming the asymmetry of the molecule at once, from previous knowledge of the characteristics of such a molecule.

The results show further that the spacings of the $(0\ m\ n)$ and $(1\ 0\ m)$ planes are halved unless $(m + n)$ and $(1 + m)$ are even. This shows that the arrangement of the molecule is as follows:

Let one of the four molecules be placed at each of the eight

corners of the cell. Let a second, which is the reflection of the first in a plane parallel to the yz face of the cell, be placed so that its projection on that face is at the centre of the face. Correspondingly, for the third molecule reflected in the xz face. The position of the fourth molecule is determined by the positions of the others.

The space group of the arrangement thus arrived at is known to geometrical crystallography: The possibility of its existence has been foretold, and the symbol C_{2v}^{10} has been assigned to it.

If the asymmetry of the molecule could neither have been proved nor assumed, there would have been an alternative to the above classification. The crystal might have been holohedral and its space group Q_h^{12} .

Geometrical crystallography could not have carried the argument so far; nor can it be of any use whatever in carrying it farther. But the point to which we wish to draw particular attention is that it is not necessary to employ the terminology of the space group theory at any stage; and in the early experiments its use would have been very confusing.

Repulsion Effect between the Poles of an Electric Arc. H. M. BARLOW. (*Phil. Mag.*, July, 1923.)—"I suggest that the evidence is in favor of the view that at least a measurable part of the repulsion effect in an arc is due to the 'pinch' phenomenon operating in the gaseous conducting column between the poles." "A conductor may be imagined to consist of a large number of filaments parallel to the axis, each carrying part of the total current. All the filaments except the one on the axis will experience a force tending to urge them toward the centre. If, therefore, the conducting column is mobile, it will contract so as to diminish its cross-section and, in consequence, increase in length. . . . Although a gas will not normally resist change of pressure, we have to remember that in the case of an arc the radial striction forces are exerted more or less uniformly along its whole length, so that the ionized vapor is kept within a confined space. The system is analogous to a rubber tube containing gas under pressure and having rigid plugs in its ends." The poles of the arc are these plugs and they are pushed apart by the filaments of current crowding in toward the axis. Other forces must be present in addition since a calculation shows that the "pinch" effect is competent to account for only 30 per cent. of the observed repulsion.
G. F. S.

An Apparatus to Demonstrate the Effect of Dust Particles, Ions and Electrons in the Production of Clouds. C. LAKEMAN and R. SISSINGH. (*Physik. Z.*, June 1, 1923.)—By this piece of apparatus a whole audience can see the path of an alpha particle that has ploughed its destructive way through a mass of air.
G. F. S.

Loss of Sunlight at Paris and in its Suburbs. L. BESSON. (*Comptes Rendus*, January 15, 1923.)—By means of Bellani's integrating actinometer a study has been made of the quantity of sunlight received directly and indirectly in summer at ten stations in or near to Paris. The results have been plotted in such a way as to bring out their relation to the direction of the wind at the time of observation. For example, at Ville Evrard, situated to the east of the capital, the light is represented in quantity by .83 when the wind is from ENE to S, while it is as .62 with a wind from the WNW. In the latter case the wind brought to the observing station the smoke of Paris, and a loss of 25 per cent. in the light was the consequence. This is due to two causes, loss of atmospheric transparency and increase of cloudiness. The importance of the first of these is proved by observations extending over a period of nine years made at Montsouris at the middle of the day in summer under a clear sky. In regard to the second it has been found at Parc Saint-Maur, 8 km. from Paris, that a wind from the direction of the city sensibly reduces the duration of sunshine by reason of increased cloudiness. The radius of the effect is at least 10 km.
G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

DYNAMOMETER TESTS OF AUTOMOBILE TIRES.¹

By W. L. Holt and P. L. Wormeley.

[ABSTRACT.]

POWER-LOSS tests have been made on a large number of tires of different makes and sizes. From a study of the results, the following conclusions can be drawn. These are based on: No tractive effort, a speed of twenty-five miles per hour, and the normal axle loads and air pressures.

(a) The average loss in $30 \times 3\frac{1}{2}$ fabric tires is 0.71 horsepower; in cord tires, 0.48 horsepower.

(b) The average loss in 4-inch fabric tires is 0.94 horsepower; in cord tires, 0.67 horsepower.

(c) As an average, the loss in cord tires is approximately 70 per cent. of that in fabric tires.

(d) Extreme cases between the highest fabrics and the lowest cords show the cord with only 40 per cent. of the loss found in the fabric.

(e) Considering only the cord tires, the lowest loss for each size of tire is about 60 per cent. of that of the highest.

From the study of the causes for these wide differences, it is found that they are largely due to variations in carcass construction. The tread has a small effect and the tube (if of standard construction) very little, if any, effect on the power loss.

A large variation is found in the size of different makes of tires of the same rated size. The oversize or undersize feature has very little effect on the power loss, but has quite a large effect on the load-carrying capacity.

The amount which a tire is deflected, due to the axle load, is not a measure of the power loss. For the same deflection, overloading produces a more severe action on a tire than under inflation.

The power required to supply that absorbed by the tires and dissipated as heat must come from the fuel used, and, accordingly,

* Communicated by the Director.

¹ Technologic Paper No. 240, price ten cents.

a change in the kind of tires or the conditions under which tires are run will manifest itself in an increase or decrease in fuel economy. It is not out of the way to attribute a difference in fuel consumption of as much as 10 to 20 per cent. to changes in tires or tire conditions.

Probably the most important feature of dynamometer tests is that they furnish a means for accurately measuring the internal friction in tires. By means of progressive tests it is possible to closely trace just what takes place inside a tire and actually measure the effect of details of design and thus aid in coördinating more closely the different parts.

THE VISIBILITY OF RADIANT ENERGY.²

IN coöperation with the Nela Research Laboratories a new determination of the visibility of radiant energy has been made by the step-by-step method, an equality-of-brightness method with little or no hue difference in the two parts of the photometric field. Between 490 and 680 $m\mu$, inclusive, measurements were made upon fifty-two observers, some of them common to previous investigations; for thirty-eight of these observers measurements were continued to include 430 and 740 $m\mu$.

Energy values were based upon radiometric and spectrophotometric measurements made at the bureau, checked by an independent color temperature measurement at the Nela Research Laboratories. Luminosity values were obtained with a Brace spectrophotometer. The step was made by moving the collimator slit. The ratios of luminosities were measured with a Brodhun variable sector. The photometric field was the divided circle type subtending an angle of 3° . Brightnesses were safely above the Purkinje region, except, perhaps, at the end regions of the spectrum.

The method and apparatus are described in detail in the paper, and the results compared with those of other investigations. The conclusions reached may be summarized as follows:

(1) The final average values obtained fall within the values obtained in other investigations, except in parts of the outer regions of the spectrum.

(2) Comparisons between individuals common to other in-

² Scientific Papers, No. 475, price fifteen cents.

vestigations show on the average the same sort of agreement or disagreement as do the final average curves. There is evidence that the visibility of some individuals varies considerably from time to time.

(3) There is no certain difference between the average values of visibility obtained by the flicker and equality-of-brightness methods, provided the former is used under the experimental conditions recommended by Ives and the latter does not depart too widely from these conditions.

(4) This does not conflict with the conclusion of Hyde, Forsythe, and Cady and others that there is a difference between the visibility curves obtained by the two methods when the usual large Lummer-Brodhun field is used for the equality-of-brightness measurements.

(5) A revision of the I.E.S. mean curve is proposed which results in better agreement with the average experimental visibility data and still gives the same wave-length centre of gravity for light of a color temperature of 2077° K., as is given by Ives' physical photometer solution.

(6) The step-by-step method of measuring visibility is a reliable method with a precision comparable with that of the flicker method and much superior to the simple equality-of-brightness method involving large hue differences.

(7) Further statistical investigations would not seem to be as important as investigations into the effect of experimental conditions such as field size and brightness upon the visibility obtained by the two common methods of photometry. The investigations along these lines conducted by Ives should be supplemented and his conclusions verified, if correct, but with the step-by-step equality-of-brightness method rather than the one involving large hue differences, and with many more observers.

TESTS OF CAUSTIC MAGNESIA MADE FROM MAGNESITE FROM SEVERAL SOURCES.³

By P. H. Bates, Roy N. Young and Paul Rapp.

[ABSTRACT.]

THE properties of oxy-chloride cement have been studied, particularly in relation to the source (or properties) of the magnesite ores, conditions during the calcining process, and various

³ Technologic Paper No. 239, price ten cents.

oxy-chloride cement mixtures. Ore from Greece, from two different sources in California, and from the State of Washington were used, as these were representative of the chief sources of supply for this country. They include two different types of ore, the first three being amorphous, and the last crystalline. Each ore was crushed and separated into three lots, differing only in size of particles. Size 1 contained the particles which passed a 1-inch screen, but was retained on a $\frac{1}{2}$ -inch screen; size 2 passed a $\frac{1}{2}$ -inch, but was retained on a No. 4 sieve; and size 3 passed a No. 4, but was retained on a No. 8 sieve. Each lot was then calcined in a 3 by 30-foot rotary kiln under fixed conditions throughout the operation. The temperature range, including all burns, was from 700 to 1100° C.

After grinding the caustic magnesia (the product from the kiln), the fineness, specific gravity, weight per cubic foot (loose and packed), loss on ignition, carbon dioxide content, and index of refraction were determined. There was difficulty in determining the fineness, particularly in the use of the No. 200 sieve, on account of the finest particles of the very active magnesias adhering to the screen or agglomerating into larger particles during the operation. There were wide differences between loose and packed weights per cubic foot, which brings out the importance of weighing caustic magnesia when making up mixtures, rather than measuring by volume as some do. Although a minimum and maximum carbon dioxide content has often been used in specifications for caustic magnesia, no relation was found between this constituent and the behavior of the oxy-chloride product. The index of refraction gives promise of being valuable in determining degree and uniformity of burning, but will not indicate changes in the material, occurring during storage, that have a marked effect on the properties of the cement. It was necessary to "age" some of the very active magnesias to make them usable.

Caustic magnesia from each lot was used in mixes prepared according to three flooring formulas, two stucco formulas, and one laboratory test formula. Only one concentration (22° Bé.) magnesium chloride solution was used for mixing with the dry materials, as this concentration is conceded to be the best for general use. Service tests were made in conjunction with the laboratory tests, and, therefore, the consistency of the wet mixture (excepting the laboratory test mix) was such as is generally used in

practice, and was kept the same in all cases, as nearly as possible. The service tests consisted of the laying of flooring panels; erection of stucco panels, all exposed to actual service conditions, and subsequent observations, including measurements of linear changes.

Three types of specimens were used in making strength tests: The briquette (of the shape used in the standard strength test for Portland cement mortar), for tensile strength; a $\frac{1}{2}$ by 2 by 13-inch bar, for transverse strength; and a 2 by 4-inch cylinder, for compressive strength. In order to get an indication of the effect of intermittent wetting and drying of the set stucco during its early life, such as the material generally receives from exposure to the weather, specimens were tested in the following manner: After storing twenty-one days in the laboratory air they were placed in water for one day, followed by one day in air under certain temperature and humidity conditions. This cycle of water and air storage was repeated twice, and after an additional day in air (making twenty-eight days in all), the strength tests were made. Also, linear changes, resulting from this treatment, were determined. The laboratory specimens for expansion tests were $\frac{1}{2}$ by 2 by 13-inch bars. The measurements were made by means of a 10-inch Berry gauge.

The results show that the various ores used require different conditions of calcination in order to produce caustic magnesia of approximately the same quality. Very light burning produces a magnesia which is too active for use in the customary oxy-chloride cement mixtures without "ageing" or the use of a retarder. An increase in the degree of calcination increases the time of set of the magnesia. Also, the degree of calcination affects, to a great extent, the strength, water resistance, and volume change of the set cement mixture. However, there are other factors which influence these properties nearly as much, if not more (within reasonable limits), than the burning. By the use of different types of aggregates with a magnesia, products, very different in behavior under test, may be obtained. Also, by changing the proportion of given aggregates, the products may be made to differ widely. Therefore, a magnesia considered good in quality may be made to give very unsatisfactory results, and one considered very poor often may be made to give excellent results.

STRESSES IN A FEW WELDED AND RIVETED TANKS
TESTED UNDER HYDROSTATIC PRESSURE.⁴

By A. H. Stang and T. W. Greene.

[ABSTRACT.]

FOR the purpose of ascertaining the relative merits of riveted, as compared with electric-welded tanks, four steel tanks, four feet in diameter and ten feet long, made of $\frac{5}{16}$ -inch mild steel plates, were tested under hydrostatic pressure. The tanks were designed for a stress of 16,000 lbs./in.² at a working pressure of 200 lbs./in.² Two of the tanks were butt-welded, one was lap-welded, and the fourth was of ordinary lap-riveted construction. The ends of the tanks were spherical, having a radius of four feet.

Strain gauge measurements were made at various portions of the tanks and at pressure increments of 50 lbs./in.² until failure. The results of the hydrostatic tests proved rather unsatisfactory as a comparison of the relative strengths of the different types of construction. Due to secondary failures, such as leaks around the fittings, the possible strength of the tanks was not reached. In fact, the secondary failures were responsible for failure in each case. In one tank the failure was at the weld around a two-inch pipe outlet; in the second, at the manhole; in the third, at the end transverse weld, and in the riveted tank at the end transverse riveted joints. The first two failures might have been obviated by better welding of the pipe fittings and manhole saddle to the shell. Extra reinforcement at the junction of the spherical end to the cylindrical shell would have reduced the stresses at the junction where the other two tanks failed. The location of the end transverse seam or riveted joint farther back on the shell of the tank would have taken this joint out of the region of high stress intensity caused by the abrupt change in direction of force at the junction of the spherical end of radius four feet to the cylindrical shell of radius two feet.

As the results of the analysis of the deformation and distribution of stress in these tanks, the following general conclusions seem warranted:

1. The commonly accepted theory for the design of tanks is, for all practical purposes, sufficiently accurate, provided the computed stresses are not influenced by secondary stresses.

⁴ Technologic Paper No. 243, price five cents.

2. For thin tanks, the measured stresses, based upon the two-dimensional formula, are in close agreement with the design stresses computed by the common-pressure formulas, provided the former are not affected by secondary causes. This is borne out by the results obtained at the centre of the end.

3. Secondary stresses resulting in high stress intensity were caused by (a) faulty design of the attachment of the spherical end to the cylindrical shell, (b) non-conformity of the shell to an accurate circular section, and (c) discontinuities in the shell for the manhole and fittings. These may produce a possibly dangerous condition if present near a welded or riveted joint or seam.

4. The stresses were increased by the presence of a seam.

UNITED STATES GOVERNMENT SPECIFICATION FOR WATER-RESISTING RED ENAMEL.⁵

THIS specification was prepared by the technical committee on paints of the Federal Specifications Board after careful consideration of suggestions from manufacturers. Highest quality red enamel suitable for outside use is called for. This consists of pure toluidine red toner in a vehicle of the very best water-resisting long oil spar varnish. A general description of the enamel is followed by detailed directions for sampling and testing, including tests for caking in container, working properties, color, hiding power, weight per gallon, coarse particles and skins, identification and determination of pigment, non-volatile matter, drying time, water resistance, and toughness.

UNITED STATES GOVERNMENT SPECIFICATION FOR GLOSS INTERIOR LITHOPONE PAINT, WHITE AND LIGHT TINTS.⁶

THIS specification was prepared by the technical committee on paints of the Federal Specifications Board after careful consideration of suggestions from paint manufacturers. Paints under this specification are not intended for outside exposure; they shall dry to gloss opaque coats that will adhere well to wood, metal and plaster, stand washing with soap and water, and show no material

⁵ Circular No. 146, price five cents.

⁶ Circular No. 147, price five cents.

change in color or exposure to light or material yellowing when kept in the dark.

A general description of the pigment, vehicle and completed paint, which is a lithopone zinc oxide pigment in a vehicle of treated drying oils or varnish, is followed by detailed directions for sampling and testing. The tests cover caking in container, color, weight per gallon, brushing properties, time of drying, resistance to washing, fastness to light, yellowing, determination of water, volatile thinner, percentage of pigment, percentage of non-volatile vehicle, nature of non-volatile vehicle, coarse particles and skins, and analysis of pigment.

Wetting of Glass and Quartz by Mercury. EARLE E. SCHUMACHER (*Jour. Am. Chem. Soc.*, 1923, **45**, 2255-2261) has attempted to cause mercury to wet glass and silica after removal of gases from the surface of the solid as completely as possible with present available means. Fairly good wetting was usually obtained in the case of quartz, but resulted only occasionally in the case of glass, becoming more difficult as the alkali content of the glass increased.

J. S. H.

Cupric Oxide Jellies. HARRY B. WEISER, of The Rice Institute (*Jour. Phys. Chem.*, 1923, **27**, 685-691), draws the following conclusions as the result of an experimental study of cupric oxide jellies. When a suitable concentration of colloid cupric oxide is precipitated at a suitable rate, a hydrous cupric oxide jelly is produced, for instance, ammonia is added to cupric acetate in the presence of a small amount of a sulphate, and the resulting colloidal solution is permitted to precipitate spontaneously. A colloid of suitable concentration does not result in the absence of sulphates. Jellies are not formed on the addition of ammonia to cupric sulphate, chloride, or nitrate, since a colloid is not formed, but a gelatinous precipitate is immediately deposited.

J. S. H.

Action of Silica on Electrolytes.—According to ALFRED FRANCIS JOSEPH and JOHN STANLEY HANCOCK, of the Wellcome Tropical Research Laboratories, Khartoum (*Jour. Chem. Soc.*, London, 1923, **123**, 2022-2025), silica reacts with an aqueous solution of sodium chloride to produce free acid and a complex silicate of low solubility, but alkaline reaction. It reacts in a similar manner with aqueous solutions of sodium sulphate, calcium sulphate, ammonium chloride, and calcium chloride. Experiments made with hydrochloric acid and with citric acid demonstrated that pure silica has no effect on the hydrogen-ion concentration of an aqueous solution of an acid.

J. S. H.

NOTES FROM THE RESEARCH LABORATORY
EASTMAN KODAK COMPANY.*

CHEMISTRY OF THE KODACHROME BLEACH.¹

By E. R. Bullock.

THIS paper is a discussion of the chemical reactions underlying the ozobrome and kodachrome processes. It is concluded that the bleach solutions act by converting the silver of the image into silver bromide, the potassium dichromate of the bleach being simultaneously partially reduced to chromic orthochromate, and the ferricyanide catalyzing this reaction. As regards the theory of catalysis in general, it is suggested that in certain instances at least an explanation may be based upon the assumption that the degree of simplicity of mechanism of a reaction is a factor in its velocity.

NOTE ON THE INFLUENCE OF CRYSTAL HABIT ON THE
PHOTOCHEMICAL DECOMPOSITION IN SILVER
BROMIDE CRYSTALS.²

By S. E. Sheppard and A. P. H. Trivelli.

IT is noted that while the visible photochemical decomposition has in common with the initiation of development the property of commencing at isolated points its further increase may be a relatively orderly process, orienting according to definite directions in the crystal. Although the growth of the photoproduct proceeds mainly by discontinuous increments, it is neither uniform, nor haphazard, but radiates along the lines of more rapid growth.

* Communicated by the Director.

¹ Communication No. 181 from the Research Laboratory of the Eastman Kodak Company and published in *B. J.*, Aug. 10, 1923, p. 491.

² Communication No. 182 from the Research Laboratory of the Eastman Kodak Company and published in *Phot. J.*, July, 1923, p. 334.

PREPARATION OF ALKYLGUANIDINES.³

By R. Phillips and H. T. Clarke.

METHYLGUANIDINE sulphate is formed in good yield from methyl iso-thiourea sulphate and methylamine in aqueous solution. Dimethylguanidine sulphate is also readily formed in the same way from dimethylamine. Methyl mercaptan is produced in the above reactions as a by-product. Its crystalline sodium salt is here described for the first time.

THE INTERFACIAL TENSION BETWEEN GELATIN SOLUTIONS AND TOLUENE.⁴

By S. E. Sheppard and S. S. Sweet.

THE relation of the orientation of specific atom groups in the molecule to the emulsoid state is discussed. Using ash-free gelatin, the separation of gelatin at a benzene-water interface was found to be affected by the presence of air. The stability of gelatin-air foam was found to be greatest at the iso-electric point. An investigation was made of the stability of gelatin-air foam as a function of hydrogen-ion concentration with the following results:

Temp. pH	30° Foam. c.c.	Half period. secs.	40° Foam. c.c.	Half period. secs.
1.29	40	45	25	30
3.80	40	50	25	45
4.34	40	75	30	90
4.58	40	150	30	120
4.78	40	180	35	150
4.82	60	180	40	180
4.87	70	300	35	180
5.00	70	300	40	180
5.10	70	300	40	150
5.20	50	300	35	90
5.39	40	240	30	60
7.60	40	150	25	60
10.30	35	90	30	45
12.20	40	60	30	30

³ Communication No. 174 from the Research Laboratory of the Eastman Kodak Company and published in *J. Am. Chem. Soc.*, July, 1923, p. 1755.

⁴ Communication No. 152 from the Research Laboratory of the Eastman Kodak Company and published in *J. Amer. Chem. Soc.*, Dec., 1922, p. 2797.

The interfacial tension between gelatin solutions of various hydrogen-ion concentration and toluene was measured at 30° C., 40° C., and 50° C. At the iso-electric point, the lowering of tension by gelatin increases rapidly. Secondary phenomena due to hydrolysis were observed.

SEPARATION OF XYLENES.⁵

By H. T. Clarke and E. R. Taylor.

A DESCRIPTION of a working method for the isolation of pure ortho, meta, and para xylenes from coal-tar. The meta isomer can be obtained in a technically pure state by fractional distillation; on treatment with hot dilute nitric acid, any ortho and para xylenes present are oxidized, and the pure meta compound is further purified by sulphonation with subsequent hydrolysis of the resulting sulphonic acid. The ortho and para xylenes cannot be obtained in nearly so high a state of purity as the meta; the preparation in pure form depends upon subjecting the appropriate fractions to selective sulphonation, followed by crystallization and selective hydrolysis of the sulphonated products. Para xylene is attacked more slowly than its isomers by concentrated sulphuric acid, and its sulphonic acid requires a higher temperature for its hydrolysis.

A PRELIMINARY STUDY OF THE PLUNGER TYPE OF JELLY-STRENGTH TESTER.⁶

By S. E. Sheppard and S. S. Sweet.

A NEW type plunger tester is described, with continuous chain increment loading and variable plunger heads. The effect of different shapes of plunger has been studied, and it is shown that a flat plunger, because the area of contact does not vary with the load, is the most satisfactory. Plungers with rounded base are unsatisfactory, producing load-deflection curves which are not straight lines. Using any diameter of plunger, the depth of jelly required should be at least 7 cm. Also, the ratio of the diameter of the plunger to the diameter of the vessel must be less than a certain value, or spurious jelly-strength values will be obtained.

⁵ Communication No. 162 from the Research Laboratory of the Eastman Kodak Company and published in *J. Amer. Chem. Soc.*, March, 1923, p. 830.

⁶ Communication No. 164 from the Research Laboratory of the Eastman Kodak Company and published in *J. Ind. Eng. Chem.*, June, 1923, p. 571.

This ratio of diameter of vessel to the diameter of plunger should be at least five. This plunger tester has been compared with the torsion type of instrument and a definite factor determined for converting jelly-strength into rigidities by the plunger method. This factor, the ratio between the rigidities as measured by the plunger method and the torsion machine, was found to be constant, using either ash-free or commercial gelatin. Jelly-strengths can be determined as accurately as viscosities and can be expressed in absolute units. The suggestion is offered that a standard type of plunger tester, with elimination of systematic errors, be agreed on by manufacturers and colloid chemists.

**MODIFICATION OF THE SPENCE-KRAUSS-HERZBERG
METHOD FOR MICROSCOPIC EXAMINATION
OF PAPER PULP FIBRES.¹**

By E. P. Wightman.

A RAPID and simple technic for use in the visual comparison method of microscopically estimating paper pulp fibres is suggested. The method described below is believed to be time saving and to have improvements over the technic described by previous workers. A sample of paper, or pulp, to be examined is well pulped in the usual way. After the tube containing the sample has been shaken, a drop or two of the pulp is transferred to a clean microscopic slide by means of a pipette with exit of wide diameter. The fibres are teased apart and allowed to dry on the slide. After the slides of the whole series to be tested are completed as well as those of the standard pulps, containing known quantities by weight of the various kinds of fibres, the fibres on each slide are moistened with water and the excess removed. One reason for drying first, and then remoistening, is to allow the fibres to stick to the glass, otherwise it is difficult to be sure whether or not a representative sample remains on the slide. When the excess moisture has been removed Herzberg zinc chloride-iodine stain and a cover glass are added, and the excess stain is squeezed out. Preparation of all the samples in hand, as a whole, rather than carrying out the complete operation on each one separately, is advised.

¹ Communication No. 168 from the Research Laboratory of the Eastman Kodak Company and published in *Paper*, Feb. 14, 1923, p. 14.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

NEW SOURCES OF SANTONIN.¹

By Arno Viehoveer and Ruth G. Capen.

[ABSTRACT.]

OF the fifty-six species of domestic *Artemisia* studied in the Bureau of Chemistry, two (*Artemisia Mexicana* and *Artemisia neomexicana*) gave distinct tests for santonin. In a third (*Artemisia Wrightii*) the presence of santonin was indicated. Thus it would seem possible to utilize domestic plants, growing as weeds in barren fields, for making santonin.

FURFURAL FROM CORNCOBS.²

II—THE BUREAU OF CHEMISTRY EXPERIMENTAL PLANT AND PROCESS FOR
FURFURAL PRODUCTION.

By Frederick B. LaForge and Gerald H. Mains.

[ABSTRACT.]

THE experimental plant in the Bureau of Chemistry used for the production of furfural from corncobs consists essentially of a pressure digester unit and a continuous column still. The cobs are digested with water and high-pressure steam, the vapors being condensed to form a dilute furfural solution which is concentrated in the column still.

Optimum operating conditions are: Pressure, 130 to 135 pounds (180° C.); ratio of water to cobs, 4:1; digestion period, two hours. The furfural yield obtained is 6 per cent. of the weight of cobs used. The column still separates from the dilute solution five to six pounds of crude (95 per cent.) furfural per hour with a 97 to 98 per cent. recovery. Small quantities of acetic acid, acetaldehyde, and methanol are by-products.

The process is simple and commercially feasible, and can be adapted to a number of agricultural wastes.

* Communicated by the Chief of the Bureau.

¹ Published in *J. Am. Chem. Soc.*, **45** (Aug., 1923): 1941.

² Published in *Ind. Eng. Chem.*, **15** (Aug., 1923): 823.

**A REPORT ON SOME OF THE NON-GLYCERIDE
CONSTITUENTS IN CRUDE COTTONSEED OIL.³**

By George S. Jamieson and Walter F. Baughman.

[ABSTRACT.]

THE acetone (or petroleum ether) insoluble portion of the settlings, which constitutes 0.1 to 0.2 per cent. of the crude cottonseed oil, contains proteoses, peptones, resin, pentosans, raffinose, and inosite phosphates. The pentosans constituted 1.74 per cent. and the raffinose 4.2 per cent. of the acetone insoluble settlings. It was estimated that these settlings contained approximately 12 per cent. of inosite phosphoric acid. The presence of xanthophyll and a wax was indicated. Resin is the only constituent as yet isolated in appreciable quantities from that portion of the original settlings which was soluble in acetone. No protein, starch or tannin could be detected. Tests made indicated that gossypetin, quercetin, isoquercetin, and quercemeritrin were absent.

WEARING QUALITIES OF SHOE LEATHERS.⁴

By F. P. Veitch, R. W. Frey, and I. D. Clarke.

[ABSTRACT.]

THE results of a comprehensive study of the wearing qualities of leather conducted by the Bureau of Chemistry indicate that (1) retanned chrome and chrome-tanned upper leathers are superior in pliability to other leathers tested; (2) certain types of fibre soles have objectionable features, but that those which do not develop such features are very durable; (3) rolled vegetable-tanned sole leathers give approximately 16 per cent. longer wear than unrolled leathers of the same thickness; (4) loading sole leathers with glucose and Epsom salts does not materially affect their serviceability; (5) chrome-tanned sole leathers, especially unwaxed chrome-tanned leather, show a strikingly longer wear than the other kinds of sole leathers tested.

The experiments were conducted with army shoes and under exceptionally dry conditions of service, which points must be fully considered in connection with the results obtained. Particu-

³ Published in *Cotton Oil Press*, 8 (Sept., 1923): 27.

⁴ Issued as *U. S. Dept. Agr. Bul.* 1168, Sept. 5, 1923.

larly should this be borne in mind with regard to sole leather loaded with glucose and salts and with regard to unwaxed chrome-tanned sole leather. While the latter was the most serviceable in the tests described, it is generally known to be unsatisfactory for outdoor wear in humid climates because of the readiness with which water goes through it. Waxing overcomes this particular defect to a large extent.

Nitrates in the United States in 1922.—A report on the production and importation of nitrates during 1922 has been issued by the United States Geological Survey, the data having been prepared by G. R. MANSFIELD.

Sodium, potassium, and calcium nitrates are widely distributed in small quantities through many of the western and southwestern states. The most promising deposits, those of the Amargosa region, in southeastern California, were studied intensively by members of the United States Geological Survey during the war, and the results of these studies have recently been published. They showed clearly that these deposits, though interesting scientifically, were quantitatively insufficient for commercial development.

The Geological Survey still receives inquiries from time to time regarding nitrate deposits, but no evidence has yet been produced to show that in any of the deposits mentioned by correspondents the nitrate is of more than scientific interest. Although fine specimens or small lots of practically pure sodium and potassium nitrates have been found at many places the quantity has always proved insignificant.

No advance can be recorded in the production of atmospheric nitrogen in the United States for 1922. A comparatively small plant in New York State uses a modification of the Haber process, but its product is in a form not suitable for use as fertilizer. The United States Government has not yet disposed of the Muscle Shoals plant, but work has been resumed on the dam, which is the key feature of the project.

Chile Nitrate.—As reported by the Bureau of Foreign and Domestic Commerce, 149,570 long tons more of nitrates were imported into the United States from Chile in 1922 than in 1921, but the imports for 1922 were still far below the average over the last ten years.

Much of the material imported into the United States between 1914 and 1919 went to manufacturers of munitions. When the demand from this direction ceased, there were large stocks on hand in the United States and at the primary markets. As a result the total shipments to Europe, the United States, and to various other parts of the world dropped tremendously in 1919. In 1920 renewed confidence was evident, and exports from Chile to the United States and Europe tripled. By the end of that year this confidence had weakened, and in

1921 imports of nitrate in Europe and in this country were again greatly reduced. No proper basis has been established on which to estimate the consuming power of Europe and the United States, but it seems probable that for these countries it now exceeds that of the years prior to 1914.

Throughout 1922 considerable dissatisfaction was expressed at the manner in which sodium nitrate is handled in Chile, where a trust backed by the Chilean Government arbitrarily fixes its prices. Consumers contend that had the trust been willing to lower prices more nitrate would have been consumed throughout the world, but there is no evidence that the Chilean Government intends to change its present plan of operations.

Imports of Inorganic Nitrogen.—Sodium nitrate made up by far the greater portion of the imports of nitrogen compounds into the United States in 1922. Chile furnished practically all of this product. Calcium cyanamid, ammonium sulphate, calcium nitrate, and part of the sodium nitrate were imported for consumption in the fertilizer industry, the potassium nitrate and the remainder of the sodium nitrate for use in the chemical industries.

Atomic Weight of Antimony.—A preliminary study of the atomic weight of antimony derived from different sources has been made by SHEIKH D. MUZAFFAR, of Cambridge University, England (*Jour. Am. Chem. Soc.*, 1923, **45**, 2009–2013). Stibnite was obtained from Hungary, Borneo, Peru, and Bolivia; and each of the four ores was used separately for the isolation of pure antimony. The antimony had the following atomic weight according to its source: Hungary, 121.14; Borneo, 121.56; Peru, 121.72; Bolivia, 122.37. The striking variation in the value of the atomic weight suggests the presence of isotopes of antimony. J. S. H.

Further Tests upon Dewar Flasks Intended to Hold Liquid Air. H. BRIGGS and J. MALLINSON. (*Proc. Royal Soc., Edin.*, Vol. 43, Part 2.)—Metal flasks alone are considered. It is only when the necks are unusually short that the invasion of heat by conduction down the neck is of any importance. "With the long slender necks usually adopted for storage vessels that source of evaporative loss is either negligibly small or actually zero." The authors point out that improvements in the flasks are to be sought, not in the use of a higher vacuum between the inner and outer vessels, but in "greater attention to the polish of the reflecting surfaces, and to the means of preserving the lustre up to the time of evacuation." It is unwise to let a flask stand empty, for then the charcoal in the vacuum lets the adsorbed air pass away. This will tarnish the reflecting surfaces, thus making them better radiators. G. F. S.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, October 17, 1923.)

HALL OF THE FRANKLIN INSTITUTE,

PHILADELPHIA, October 17, 1923.

MR. CHARLES DAY, Vice-president, *in the Chair.*

The Board of Managers submitted their report. The report recorded the election of the following Resident Members:

William H. Balls, Esq.,

1422 Snyder Avenue,

Philadelphia, Pennsylvania.

Renshaw Borie, Esq.,

District Manager,

McClellan and Junkersfeld, Inc.,

Philadelphia, Pennsylvania.

Alexander Brown Coxe, Esq.,

Agriculturist,

Paoli, Pennsylvania.

Carleton Dean Haigis, Esq., D.Sc.,

Research Physicist,

Victor Talking Machine Company,

Camden, New Jersey.

Mrs. Selina Emma Peacock,

Organist,

Philadelphia, Pennsylvania.

Harold Pender, Esq., Ph.D.,

Dean, Moore School of Electrical Engineering,

University of Pennsylvania,

Philadelphia, Pennsylvania.

John Wagner, Esq.,

Philadelphia,

Pennsylvania.

Daniel Dorsey Wolf, Esq.,

Treasurer, C. C. Kampton and Sons, Inc.,

Philadelphia, Pennsylvania:

the following Non-resident Members:

W. G. H. Finch, Esq.,

Radio Editor and Engineer,

International News Service,

New York City, New York.

George F. Kunz, Esq., D.Sc., Ph.D.,
 409 Fifth Avenue,
 New York City, New York.

Israel Maizlish, Esq., Ph.D.,
 Professor of Physics,
 Lehigh University,
 Bethlehem, Pennsylvania.

Alfred Oberle, Esq., Ph.D.,
 Research Chemist,
 Universal Oil Products Company,
 Chicago, Illinois.

Archie Dayton Power, Esq., Ph.D.,
 Professor of Physics,
 University of Minnesota,
 Minneapolis, Minnesota.

Richard H. Ranger, Esq., B.S.,
 Radio Engineer,
 66 Broad Street,
 New York City, New York.

V. A. Suydam, Esq., B.S., Ph.D.,
 Professor of Physics,
 Beloit College,
 Beloit, Wisconsin.

John Widmeyer, Esq., B.S.,
 Metallographist,
 Lancaster, Pennsylvania.

William Wilson, Esq., B.A., D.Sc.,
 Engineer,
 Western Electric Company,
 New York City, New York;

and the following Associate Members:

Frank R. Garman, Esq., B.S.,
 Engineering Assistant,
 Bell Telephone Company,
 Philadelphia, Pennsylvania.

Tobias Wagner, Esq.,
 Philadelphia,
 Pennsylvania;

and additions to the library by gift, 3529 volumes, 520 pamphlets and 1 drawing; by purchase, 94 volumes and 1 pamphlet, and by binding 298 volumes.

A report of progress was presented by the Committee on Science and the Arts.

The Chairman then announced that the next business of the meeting would be the presentation of the Elliot Cresson Medal to Raymond D. Johnson, for his invention of the "Johnson Hydraulic Valve," and recognized Mr. Benjamin

Franklin, Chairman of the Sub-committee of the Science and Arts Committee investigating the device.

Mr. Franklin said, "Mr. Chairman: The construction of large hydraulic and hydro-electric plants, involving either a high head or a large volume of water, has necessitated the design of a valve which would easily and safely control the flow of water.

"Mr. Raymond D. Johnson, the inventor of the Johnson Hydraulic Valve, has successfully solved this problem by employing the principle of the needle valve in controlling the flow of water in conduits under pressure perfecting a valve which is under complete control, either automatically, by hand, or by electrically operating at a distance, and which does not deform under operative strains. Valves of this type have been constructed which control the flow to a 37,500 H. P. hydraulic turbine, having a diameter at the inlet of twenty-one feet.

"The Sub-committee of the Committee of Science and Arts of The Franklin Institute, after a careful examination and a comparison with other types of valves at present commercially available, reached the conclusion that the Johnson Valve has the following notable characteristics:

- (1) Great mechanical strength due to the cylindrical shape of all parts.
- (2) Durability, as there are no sliding contacts under pressure and the plunger in operation is unbalanced only enough to move it.
- (3) Tightness against leakage in the closed position.
- (4) Powerful hydraulic operating forces within the valve to insure opening or closing under all conditions, without recourse to external sources of power.
- (5) Simplicity of control, by hand or by electric means at a distance.
- (6) Automatic closing feature which positively insures closing of the valve in case of a break below the valve, thus greatly reducing the danger of loss of life and property damage, which invariably follows such accidents.

"The report of the General Committee concludes as follows:

"'In consideration of the ingenuity and soundness of the design, excellence of construction and operating characteristics; successfully meeting the demands of commercial requirements, The Franklin Institute awards its Elliot Cresson Medal to Raymond D. Johnson, of New York, for his Hydraulic Valve.'"

The Chairman presented the medal and accompanying documents to Mr. Johnson, who thanked the Institute for the high honor conferred upon him.

The Chairman then introduced Dr. Arthur L. Day, Director of the Geophysical Laboratory and Chairman, Advisory Committee in Seismology, Carnegie Institution of Washington, who presented the paper of the evening on "Earthquakes and Volcanic Eruptions."

The speaker gave some of the results of the study of earth movements in California, obtained through accurate triangulation, for the determination of surface changes. He also gave a summary of the investigations conducted by the Carnegie Institution of Washington, of the destructive earthquakes in Chile, in November of last year, and by means of colored slides, illustrated the differences between the earth movements in California and in Chile. References

to volcanic phenomena were largely confined to recent eruptions of Etna, of which a number of colored slides were shown, portraying various stages of the several eruptions.

After a brief discussion a vote of thanks was extended to the speaker.
Adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, October 3, 1923.)

HALL OF THE INSTITUTE,
PHILADELPHIA, October 3, 1923.

MR. W. H. FULWEILER, *in the Chair.*

The following reports were presented for final action:

No. 2800: Work of William Gaertner in the Design and Manufacture of Scientific Instruments. Howard N. Potts Medal to Mr. William Gaertner, of Chicago, Illinois.

No. 2808: Pneumercator. Edward Longstreth Medal to Mr. Harry S. Parks, of Philadelphia, Pennsylvania.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, October 10, 1923.)

NON-RESIDENT MEMBERS.

DR. ALFRED OBERLE, Research Chemist, 343 South Oak Park Avenue, Oak Park, Illinois.

DR. GEORGE F. KUNZ, President, The American Scenic and Historic Preservation Society, Old Tribune Building, 154 Nassau Street, New York City, New York.

CHANGES OF ADDRESS.

MR. ROBERT ATKINSON, Box 153, New York University, University Heights, New York City, New York.

MR. J. SNOWDEN BELL, 149 Broadway, New York City, New York.

MR. C. O. BILLOW, 1431 Jarvis Avenue, Rogers Park, Chicago, Illinois.

MR. JOHN IRWIN BRIGHT, Devon, Pennsylvania.

JOSEPH H. BURROUGHS, Esquire, 612 Bullitt Building, Philadelphia, Pennsylvania.

MR. ERNEST H. DAVIS, 901 Vine Avenue, Williamsport, Pennsylvania.

MR. J. H. GRANBERRY, in care of American Can Company, Boston and Hudson Streets, Baltimore, Maryland.

MR. EDWARD W. HAMMER, 55 John Street, New York City, New York.

MR. WILLIAM H. HARDING, 1127 Land Title Building, Philadelphia, Pennsylvania.

- MR. GEORGE E. KINNIER, 94 Broad Street, Woodbury, New Jersey.
MR. GEORGE MACLEAN, Port Washington, New York.
MR. T. C. MARTIN, 32 Grove Avenue, Larchmont Manor, New York.
MR. ALLEN I. MYERS, 565 West 113th Street, New York City, New York.
COLONEL SAMUEL REBER, Rochambeau Apartments, Washington, D. C.
MR. H. N. SPICER, 247 Park Avenue, New York City, New York.
MR. W. H. SUPPLEE, in care of The S. S. White Dental Manufacturing Company, Unity and Oakland Streets, Frankford, Philadelphia, Pennsylvania.
PROFESSOR V. A. SUYDAM, 1126 Porter Avenue, Beloit, Wisconsin.
MR. WILLIAM R. WEBSTER, 3818 Chestnut Street, Philadelphia, Pennsylvania.
MR. ROY V. WRIGHT, in care of Railway Age, 30 Church Street, New York City, New York.
MR. C. H. ZEHNDER, Room 3018, 120 Broadway, New York City, New York.

NECROLOGY.

- MR. E. G. BASHORE, The Texas Company, Port Arthur, Texas.
MR. H. W. BIDDLE, 424 Chestnut Street, Philadelphia, Pennsylvania.
MR. THOMAS DE WITT CUYLER, Arcade Building, Philadelphia, Pennsylvania.
MR. WILLIAM J. HAINES, 1011 Chestnut Street, Philadelphia, Pennsylvania.
MR. ROBERT W. HUNT, 2200 Insurance Exchange Building, Chicago, Illinois.
MR. A. STEIN, 97 Gold Street, New York City, New York.

LIBRARY NOTES.

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BOOK REVIEWS.

LABORATORY DIRECTIONS IN INORGANIC CHEMISTRY. By Alexander Silverman, University of Pittsburgh. Second edition, revised. 56 pages, 4to. D. Van Nostrand Company, New York. Price, \$1.25.

Works of this character are best employed by those who prepare them. Many such manuals are on the market, and each reflects to a dominant extent the method which the writer has adopted after considerable experience. It is usually unsatisfactory for a laboratory teacher to use any but his own manual. The book in hand has doubtless given satisfaction to large numbers of students,

and seems to be fully equal to the generality of works of its class. Herbert Spencer said that education does not form character, and his dictum finds application every day in the work of students in the elementary laboratory, for no amount of talking will secure universal care in managing apparatus. Bunsen burners will be allowed to have too much air, stoppers of bottles will be laid on dirty tables and many other minor sins committed against the principles of good chemistry. This book contains a large number of items of advice as to care and cleanliness. How far the teacher gets the student's obedience is not known. Minute examination of the book might show points on which instructors would differ, but in the main the data are correct and clearly expressed. In the preparation of oxygen with the mixture of potassium chlorate and manganese dioxide the quantity of the latter is as usual too large. Twenty-five per cent. of the dioxide is quite sufficient for the action. It is a question whether this catalyst may not be advantageously replaced by ferric oxide. The latter acts quite well in proportion of 25 per cent., and being bright red it cannot be confused with antimonous sulphide or charcoal, dangers to which the manganese compound is liable. Moreover a good grade of ferric oxide is now obtainable at a lower cost than a good grade of the manganese compound. It is evident that the book is intended to be used with a general textbook or with lecture notes. The illustrations deserve some animadversion. In common with those generally seen in elementary manuals, they are rather sketchy. The time has now arrived when the methods photo-engraving give, at moderate cost, excellent reproductions of actual apparatus, and the modern laboratory should no longer be supplied with makeshift materials. In this book, for example, the student is advised to put a stopper in the sink and use it for a pneumatic trough! Worse advice could hardly be given.

HENRY LEFFMANN.

ALLOYS RESISTANT TO CORROSION: A summary of papers and discussions at a joint meeting of the Faraday Society and the Sheffield Section of the Institute of Metals. Pamphlet, reprinted from the *Transactions of the Faraday Society*, 8vo, 75 pages.

This pamphlet is filled with most interesting and valuable data. The corrosion of metals and alloys has great practical importance; any information concerning its causes and prevention is welcome to many branches of industry and to those interested in the household affairs. On the latter feature should be mentioned a report on a new silver alloy which does not tarnish. English standard silver is, as is well known, sterling, that is, only one-twelfth alloy ($7\frac{1}{2}$ per cent.). The British government will not "hall-mark" any other silver alloy. The new alloy is of this standard. In the preliminary report no statement is given as to the composition of the diluting metal, but, of course, this cannot be kept secret after the material comes into the market, though even then some special method of mixing may be held in confidence by the makers so that a monopoly may be maintained. The new alloy will be a great boon to those who delight in silver service at the table, for the manufacturer's agent reports that he has kept the ware in his house in use for two years without polishing. Considerable space is given to some of the iron alloys, such as the stainless steel and iron, which have become familiar in cutlery. Nickel-chromium alloys also receive attention. One paper is devoted to the "dry corrosion" of metals, that corrosion in which there is no direct contact with

water, but exposure to air. As might be expected, it is found that acid and alkaline vapors have marked action, sulphurous acid being dangerous to iron and nickel, ammonia to copper and hydrochloric acid to zinc and aluminum.

The pamphlet will well repay careful reading by all interested in practical use of metals and alloys.

HENRY LEFFMANN.

DISCOURS DE LA NATURE DE L'AIR, etc. Par Edma Mariotte. 118 pages, 12mo. Paris, Gauthier-Villars et Cie., 1923. Price, 3 Francs.

This is a volume of the series of reprints of the original communications of eminent French scientists of earlier days—Masters of Scientific Thought, is the specific title of the series. The name of Mariotte is indissolubly connected with physical chemistry, by reason of his discovery of the law of gas-pressure. Boyle shares with him, indeed, honor in this matter, but the preference has generally followed chauvenistic tendencies, for British writers almost always speak of Boyle's law and French writers of Mariotte's law. American writers are apt to avoid the issue, and speak of the law of "Boyle and Mariotte." In accordance with French custom, the book has no index and a small "Table des Matières" at the back. A general statement is given of the object of the series and of the value of re-reading the works of the masters, then follows a biography of Mariotte, from which we learn that the data of his early life are somewhat scanty. He was born in Burgoyne about 1620 and lived a long while at Dijon, where he entered the church. In 1666 he was appointed as physicist at the Academy of Sciences, a position for which he was well qualified. This reprint of his works includes a discourse on the nature of the air, on the vegetation of plants and a "new discovery touching sight," which is an account of his discovery of the "blind spot" in the eye. These volumes are interesting reading, and seem to the reviewer to be especially suitable for students in chemistry and physics who have advanced in modern language study far enough to read French fairly well. The text is excellent and the story interesting and instructive.

HENRY LEFFMANN.

CHEMICAL CALCULATIONS. By R. Harman Ashley, Tufts College. xi-276 pages, 12mo. New York, D. Van Nostrand Company. Price, \$3 net.

A work of this character that has reached a third edition needs little more than the announcement of its appearance. It is evident that it has met a wide acceptance and has been found satisfactory. A few errors are almost certain to creep into the first issue, but practical use by others than the author will soon detect these and they will be duly corrected. The work covers a wide field and enters into both elementary and advanced problems. Those who have large experience with students know how few are really ready with numbers. It is often astonishing how the student will go wrong on the simplest arithmetical calculation. In the present edition a great deal of attention has been given to logarithms, an addition that is very welcome in view of the increasing use of the logarithmic methods in chemistry and physics. The peculiar symbolism of hydrogen-ion concentration is very puzzling to anyone who has not a ready understanding of this method. The book is clearly printed, a matter of importance when figures are so largely used.

HENRY LEFFMANN.

YOUNGKEN'S PHARMACEUTICAL BOTANY. By H. W. Youngken, M.S., Ph.D., Professor of Botany, Pharmacognosy and Materia Medica, Massachusetts College of Pharmacy. Fourth edition, revised and enlarged, 63 illustrations and a glossary. xix-538 pages, 12mo. P. Blakiston's Son and Company, Philadelphia. Price, \$4 net.

Professor Youngken's skill in laboratorium and scriptorium is so well known that any book by him will be recognized at once as competent. The present one, being a fourth edition, needs only the announcement of the publication. It contains in a compact form a large amount of information. The student of pharmacy is especially interested in botany. It is true that modern medicine has done away to a large extent with the use of the "simples that have virtue," and substituted concentrated and synthetic drugs, but enough still remains to need careful study. For such study, Doctor Youngken's book is eminently fitted. It is a manual of technic as well as of descriptive morphology, liberally illustrated with excellent drawings and photographs. As a preliminary to the study on pharmacognosy, it is highly commendable. The author, long known for his work in Philadelphia, has now gone to the "Hub," and will continue his original investigations and writings there. Boston's gain is Philadelphia's loss.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 172, Dynamic Stability as Affected by the Longitudinal Moment of Inertia, by Edwin B. Wilson. 8 pages, quarto. Washington, Government Printing Office, 1923.

In a recent technical note (No. 115, October, 1922) of the Committee, Norton and Carroll have reported experiments showing that a relatively large (15 per cent.) increase in longitudinal moment of inertia made no noticeable difference in the stability of a standard S. E. 5A airplane. They point out that G. P. Thomson ("Applied Aeronautics," page 208) stated that an increase in longitudinal moment of inertia would decrease the stability. Neither he nor they make any theoretical forecast of the amount of decrease. Although it is difficult, on account of the complications of the theory of stability of the airplane, to make any accurate forecast, it may be worth while to attempt a discussion of the matter theoretically with reference to finding a rough quantitative estimate.

PUBLICATIONS RECEIVED.

A Textbook of Intermediate Physics, by H. Moore. 824 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1923. Price, \$9.

The Elementary Principles of Lighting and Photometry, by John W. T. Walsh with a foreword by Sir J. E. Petavel. 220 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1922. Price, \$4.50.

Advanced Practical Physics for Students, by B. L. Worsnop and H. T. Flint. 640 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1923. Price, \$8.

Chemical Engineering Catalogue, 1923 (eighth annual) edition. 1056 pages, illustrations, quarto. New York, The Chemical Catalog Company, Inc. Leased at \$2 per copy.

Chemical Calculations, by R. Harman Ashley. Third edition, revised. 276 pages, 12mo. New York, D. Van Nostrand Company, 1923. Price, \$3 net.

Pharmaceutical Botany. A textbook for students of pharmacy and general science, by Heber W. Youngken. Fourth edition, revised and enlarged. 538 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, \$4.

Alloys Resistant to Corrosion. A general discussion held jointly by the Faraday Society and the Sheffield Section of the Institute of Metals, April, 1923. Reprinted from the *Transactions of the Faraday Society*, July, 1923. 75 pages, illustrations, 8vo. London, 1923. Price, 5 shillings 6 pence, net.

L'Idée de la Théorie de la Relativité, par H. Thirring. Traduit de l'Allemand par M. Solovine. 186 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1923. Price, in paper, 8 Francs.

Laboratory Directions in Inorganic Chemistry, by Alexander Silverman. Second edition, revised. 55 pages, illustrations, quarto. New York, D. Van Nostrand Company, 1923. Price, \$1.25 net.

Technical Books of 1922. A selection. 28 pages, 16mo. Brooklyn, New York, Pratt Institute Free Library, 1923.

National Advisory Committee for Aeronautics. Technical Notes, No. 153, Analysis of Dr. Schaffran's Propeller Model Tests, by Max M. Munk. 5 pages, diagrams, quarto. No. 157, An Impulse Motor for Driving Recording Instruments, by W. F. Joachim. 13 pages, illustrations, diagrams, photograph, quarto. No. 159, The Time Lag and Interval of Discharge with a Spring Actuated Fuel Injection Pump, by Robertson Matthews and A. W. Gardiner. 16 pages, diagram, quarto. No. 160, Fittings and Other Structural Parts of Airplanes, by P. Eydam. 12 pages, illustrations, quarto. Washington, Committee, 1923.

Engineering Education and American Industry. Special Report No. 25, National Industrial Conference Board. 25 pages, illustrations, 8vo. New York, Board, 1923.

Colors Shown by Rotating Discs When Illuminated by Two Sources of Light. A. STEICHEN. (*Physikal. Zeit.*, March 1, 1923.)—A disc with adjacent white and black portions is rotated. Let it be illuminated intermittently by light from an arc lamp that passes through holes in the periphery of another rotating disc so timed in speed that the first disc shall appear to be at rest. Then the black parts of the chief disc appear black while the white parts assume the color of the light from the arc. Now let a dim incandescent lamp shine upon the disc, so that it is lighted by a steady as well as by an intermittent source. The white parts of the disc take on a color similar to that of the arc light and the black portions appear to be of the complementary color, no matter what color be given to the light from the arc. This effect is connected with the formation of colored shadows.

G. F. S.

A SERIES of demonstration experiments in the field of radioactivity is given in *Physikalische Zeitschrift*, March 15, 1923, by P. Ludwig, Freiberg, Saxony.

G. F. S.

CURRENT TOPICS.

Investigations on X-rays by the Cloud Method. C. T. R. WILSON. (*Proc. Royal Soc.*, A724.)—The distinguished originator of this method of investigation returns to the experimental problem armed with all the skill that his long previous experience has given to him. Moist air is traversed by a beam of X-rays. From the atoms beta particles are ejected under the influence of the X-rays. These rapidly moving particles come into collision with atoms from which they set ions free. When the air is already supersaturated with water vapor by reason of having been suddenly expanded from its original volume, each ion becomes a nucleus for the condensation of a portion of the vapor. Thus the track of the beta particle becomes manifest through the succession of tiny drops condensed along its path. To bring about the needed actions three pendulums were released at the same time. The first at the lowest point of its swing opened communication between the moist air chamber and a vacuum, thus causing rapid expansion. The second sent a Leyden jar discharge through an X-ray tube from which a beam traversed the expanded air. The third sent a discharge through a mercury vapor tube, the light from which was used to photograph the tracks in the damp air. By the adjustment of sliding weights on these pendulums the operations were made to succeed one another at the proper interval.

Stereoscopic photographs were taken with two cameras having their axes at a suitable angle. "An inspection of the picture shows at once (1) the point of origin of each beta ray, (2) its initial direction (*i.e.*, the direction in which an electron has been ejected from its parent atom by the action of the radiation), (3) the total length of its path or range, (4) the form of the track, its sudden or gradual bends, and the number and direction of emission of any secondary beta rays (branches), and (5) the variation of the ionization along the track; under favorable conditions the number and distribution of the ions along the tracks may be obtained by direct counting."

The twenty-two figures appended are of remarkable clearness and beauty. It will be strange if the questions they have raised followed by the answers given do not greatly help in unravelling the process of the emission of a beta particle when a quantum of energy is absorbed from an X-ray.

G. F. S.

Boundary Lubrication—the Latent Period and Mixtures of Two Lubricants. W. B. HARDY and IDA DOUBLEDAY. (*Proc. Royal Soc.*, A724.)—In general when a lubricant is applied to a solid surface the value of the friction diminishes as time passes until a steady condition is attained. The name "latent period" is given

to the time during which the diminution continues. "The latent period seems to be merely the time occupied in the orientation of the molecules of the lubricant at the solid face. The carbon chains of fatty acids, or alcohols, are loaded at one end with the -COOH or -OH groups, respectively. They may, therefore, be likened to rods loaded at one end. Placing a pool of fluid upon a surface is like flinging at it a handful of such rods grasped at random. Some will hit and stick by the loaded ends, others by the unloaded ends. The rods may be supposed to be attracted to the solid more strongly by their loaded ends, and the process of evaporation into the overlying fluid and condensation from it will increase the proportion of rods sticking to the solid face until a steady state is reached." "The proof that this view of the latent period is correct lies in one significant and striking fact, which seems to us to be open to no other interpretation. It is that molecules composed of a chain of carbon atoms, both ends of which are alike, do not manifest a latent period. Normal paraffins are such substances. In their case the rods are unloaded, and no matter how applied to the surfaces the first recorded value of the friction is the same as the last."

In the following data both plate and slider were of glass with heptioic acid as the lubricant. The latent period was forty-five minutes long, when a considerable amount of the acid was put on the plate and the slider was at once placed in it. The period lasted only ten minutes when both plate and slider were covered with lubricant, left in this condition for three hours and then brought together. When saturated vapor was passed for three hours into a chamber containing the plate and slider separated from each other, the latent period was five minutes in length after the slider was put upon the plate. In all these three cases the final value of the coefficient of friction came out the same. Temperature has a marked effect on the length of the latent period. For one set of conditions it had the values 45, 15 and 5 minutes at the temperatures 15° , 48° and 72° C., respectively. Stirring a pool of lubricant on the plate with the slider likewise shortens the latent period.

G. F. S.

Airplane-bombing Tests on Battleships.—Much interest was awakened some months ago by the newspaper accounts of the sinking of the battleships *Virginia* and *New Jersey* by bombs dropped by airplanes. Many considered the results as indicating that the battleship is wholly out of date, but others held that the attack on undefended vessels was no positive trial of the method. The U. S. Air Service has now issued a pamphlet containing authentic reports of the methods and results of these tests, being a complete transcript of the address of Major-General Mason M. Patrick, Chief of the Air Service, on September 13th last, before the Military Order of the Veterans of the World War at Washington. The address began by a quotation from the writings of Francesco Lana, who, in 1670, expressed the possibility that aircraft could be the means of destroying cities and ships. General Patrick then traced the developments

within recent years, alluding briefly to Zalinski's dynamite gun, which he stated was a failure, and to the efforts of the Germans to utilize dirigibles in attacks on cities. In the attacks on London and Paris a good deal of damage was done, but no attempts seem to have been made to attack ordinary war vessels, although a few were made on submarines. After the war, the army and navy of the United States took up the problem of the possible destruction of war vessels by airplanes. The first experiments were on two German ships that had been surrendered to the United States on condition that they would be destroyed and on the *Alabama*. These ships were destroyed and the tests were regarded by many as showing no battleship so far constructed was safe against well-operated airplanes. The Air Service does not, however, declare the battleship obsolete. The following paragraphs are from the report of General Patrick's address:

"Only a few days before the actual tests, the War Department directed that the first bombing should be done at a height of not less than 10,000 feet. We did it, but there is no other air service organization in the world that could have done the same thing. We sent our planes not to 10,000 feet, but to 11,200 feet, each of them carrying more than 2000 pounds of bombs. To do this we had to use superchargers. When a man climbs to a considerable height he finds difficulty in breathing. The percentage of oxygen in the air is less and without artificial aid he cannot exercise his full power. A motor acts in precisely the same way. The Liberty motor gives about 400 H. P. at sea level. In the rarer air at considerable distances above the earth this power falls off rapidly. The supercharger, in simple terms, is merely an air-pump which condenses this rarer air and feeds it into the motor at sea level density, thus the power of the motor can be sustained. By the way, it was with such a supercharged motor that Macready attained a height of nearly seven miles, an altitude record which stood for some time, although I believe that a Frenchman has just bettered it by a few feet."

"The first attack was made at a height of over 10,000 feet. The planes with their loaded bombs left Langley Field early in the morning, each carrying four 600-pound bombs. They flew about 170 miles, passed through three rainstorms, came out over the *New Jersey*, released their projectiles, and of the twenty which were launched, not less than four from this great height made direct hits upon the vessel's deck. That was exceedingly good practice. The two attacks upon the *New Jersey* were followed by an attack with 1100-pound bombs upon the *Virginia*. One of these struck square on the deck. The three funnels and two masts were swept away and much other damage was done. It is scarcely conceivable that any personnel on the deck would have been left alive. Almost immediately after this hit a bomb fell close alongside and inflicted a fatal blow. Just six minutes and thirty-five seconds after that particular bomb left the airplane the *Virginia* disappeared beneath the waves."

"Another thing to be remembered is that conditions for this bombing were exceedingly favorable. We knew precisely where the

boats were anchored, the sea was perfectly calm, the visibility excellent. Of course, there was no opposing fire from the vessels. As a matter of fact, the Air Service does not greatly fear anti-aircraft fire from ships. There will almost always be some motion of the vessels to interfere with the accuracy of such fire and we believe that at best its effect will be to keep the airplanes somewhat higher.

"Furthermore, even though we have losses, and in war such must be expected, we are satisfied that the damage we can do will more than offset them. Again, it may be stated with confidence that the defense against an air attack is an opposing air force. The navy hereafter must rely upon aircraft with the fleet to protect it from hostile airplanes. To provide for our national defense we must then have an adequate air force. Airplanes that scout far out to sea could from their height readily detect the approach of a hostile expedition. Remember that at a height of 5000 feet the visible horizon is 100 miles away. At 10,000 feet it is 150 miles away and the air-man from this elevation sees over a water area of about 60,000 square miles. Remember, too, that the speed of the airplane is from four to five times as great as the ordinary speed of vessels. If a hostile fleet is discovered from 200 to 300 miles off shore, the aircraft can report its presence by radio or can return to its base and give warning. Normally it would take such a fleet ten to fifteen hours to reach the vicinity of its attack. In one-half that time, from properly chosen concentration points, an air force could be assembled to meet the coming attack."

H. L.

Earthquake Records and Tidal Waves. (U. S. Department of Agriculture, Clip Sheet No. 277, October 15, 1923.)—While seismological or earthquake records can not be used directly in predicting quakes, they have other practical uses. When these records are collected and studied they throw a great deal of light on the nature of earthquakes generally, and it is conceivable that at some future time this information may lead to successful methods of prediction.

In one way, however, which is illustrated in the practice of the Hawaiian Volcano Observatory, conducted by the Weather Bureau of the United States Department of Agriculture, seismological records are of immediate practical utility. Severe earthquakes within oceanic areas frequently are attended by so-called tidal waves. There may be an interval of many hours between the occurrence of the quake and the arrival of the destructive oceanic wave at any given place. When a violent earthquake appearing to have occurred in the Pacific Ocean is registered at the Hawaiian observatory, the officials send out warnings by cable or otherwise to the regions likely to be affected by the accompanying tidal waves, so that the people may not be caught unprepared. This service is said to have resulted in a great saving of life and property.

Carbon Dioxide as a Refrigerant. J. H. PRATT (*Ice and Refrig.*, 1923, 65, 141-143) has made a study of carbon dioxide as a refrigerant and draws the following conclusions: "Briefly summing up the advantages and disadvantages of carbon dioxide, as compared with other refrigerants, it is generally believed that its use will become more and more popular, as the great advantage of safety, coupled with the fact that the operating efficiency is practically as good as other mediums, more than overcomes the imaginary difficulties with the higher pressures, particularly when operated in northern climates with ordinary cooling water temperatures." J. S. H.

New Indicators.—BARNETT COHEN, of the Hygienic Laboratory, U. S. Public Health Service (*Pub. Health Reports*, 1923, 38, 199), describes five new indicators of the sulphonephthalein series. Meta cresol purple (*m*-cresol sulphonephthalein) changes from red to yellow in the P_H range 0.5 to 2.5, and from yellow to purple in the P_H range 7.6 to 9.2. Brom-chlor phenol blue (Dibromodichlorophenol sulphonephthalein) changes from yellow to blue in the P_H range 3.2 to 4.8. Brom cresol green (Tetrabromo-*m*-cresol sulphonephthalein) changes from yellow to blue-green in the P_H range 4.0 to 5.6. Chlor phenol red (dichlorophenol sulphonephthalein) changes from yellow to red in the P_H range 5.0 to 6.6. Brom phenol red (dibromophenol sulphonephthalein) changes from yellow to red in the P_H range 5.4 to 7.0. J. S. H.

AT INTERVALS there is issued a yellow paper-covered volume of the *Proceedings of the Royal Institution of Great Britain*. It is safe to say that no other group of a few hundred pages contains so much thoroughly up-to-date scientific information in so delectable a form. The most recent number contains a report of the lectures delivered at the Royal Institution in 1920. In the first Sir Charles Parsons tells how a temperature of more than $15,250^{\circ}$ C. was obtained and outlines a method of producing a pressure, instantaneous to be sure, of 7000 tons per square inch. Under the caption "Problems of Lubrication," W. B. Hardy makes this statement: "If a glass vessel, such as a bottle, be placed upon an inclined pane of glass at a certain angle, it slips smoothly down. The glass plate is an ordinary plate cleaned with a cloth. In the usual sense of the word the surface of the plate is not lubricated, the surface is 'dry.' The lower half of the plate is then wetted with water and the bottle is now found to slip on the unwetted part, and to be sharply pulled up by friction when it reaches the wetted part. It is not sufficient, therefore, to interpose a liquid film between solid faces to get lubrication. . . . Here is another plate picked up at random in the laboratory of the Royal Institution. Its composition is unknown. Tested in the same way, water has no detectable influence on the friction between the glass and the surface of the plate. It will be well to confess at once that these simple experiments raise questions which are as yet without an answer." "Low

Temperature Studies," Sir James Dewar; "The Gyrostatic Compass," S. G. Brown; "The Scientific Work of the Late Lord Rayleigh," Sir J. J. Thomson; "Crystal Structure," W. L. Bragg; "The Thermionic Valve in Wireless Telegraphy," J. A. Fleming; "Blue Sky and the Optical Properties of Air," Lord Rayleigh; "The Menace of Man's Dispersal of Insect Pests," H. M. Lefroy—all these find a place. Less rigidly scientific, but not less interesting, is the lecture on "String Figures" the string figures we all held on our hands years ago, wherein we learn that there is a whole book on the subject. Edward McCurdy presents Leonardo da Vinci as a rare combination of the artist, the scientist and the technician. And how modern was he! "He contemplated the use of poisonous gas or powders in naval warfare for the purpose of suffocating the enemy, and told how to make a simple preventive mask. He also contemplated the contingency—as happened on occasions in Flanders—of an adverse wind causing the poison to recoil upon the users." G. F. S.

Short Sound Waves. KONSTANTIN PALAIOLOGOS. (*Zeit. f. Physik.*, Jan. 9, 1923.)—Following the plan of Martens the sound waves were obtained from a direct current arc on which was superimposed a weaker alternating current. The resulting current never fell to zero but possessed a series of maxima to each of which there was a corresponding maximum of gas pressure. In this way the arc sent out a succession of condensations. The lengths of the emitted waves were measured by means of an acoustical grating and for these experiments ranged from 1.71 to .17 mm. Every time that a sound wave was emitted there was at the same instant an electrical wave started, the length of which was found from a wave meter. The two kinds of waves, the electrical and the acoustical, have the same frequency and the lengths of both were determined as already stated. The velocities would then be in proportion to the respective wave-lengths, and since the velocity of the electric wave is known, the velocity of the sound wave can be calculated. When this was done it appeared that no change in velocity could be detected for a change in wave-length from .17 mm. to ten times as much.

G. F. S.

Atmospheric Dust. (Clip Sheet, U. S. Department of Agriculture, No. 274.)—Visibility is a large factor in air flight and in various surface operations, especially navigation. A knowledge of conditions governing visibility is therefore of considerable importance. Dustiness or mistiness may be due to incomplete combustion of coal or other fuels, seen as smoke at lower levels. Some dust particles come from volcanoes. Some, it is thought, may come from interplanetary spaces.

The Weather Bureau of the United States Department of Agriculture was provided with an instrument for measuring atmospheric dust, known as a dust counter, by the section of meteorology of the

International Union of Geodesy and Geophysics in Rome, in May, 1922. A dust count has been taken daily during the past year by the Weather Bureau from the surface at Washington, D. C., and from the top of the Washington Monument. The War Department has also permitted aviators at Bolling Field to coöperate with the Weather Bureau, taking tests at different levels, from 1000 feet to 10,000 feet above ground.

The dust counter used collects the dust from a known volume of air and deposits it on a small and very thin glass disc, where by means of a powerful microscope the particles can be counted and their character determined. Tests have shown about 90 dust particles per cubic centimetre on a very clear, dry day and as high as 933 per cubic centimetre on one day of limited visibility, but with the same dry condition of the air which prevailed on the former occasion.

R.

Anomalous Magnetic Permeability of Nickel and Steel Wires in Weak Alternating Fields of High Frequency. B. W. WEDENSKY and K. THEODORTSCHIK. (*Physikal. Zeit.*, May 15, 1923.)—Wires of 15 cm. length and of a few hundredths mm. in diameter were subjected to the fields of rapidly alternating currents of wave-lengths ranging from 54 to 585 m. The permeability of both nickel and steel varies in a complicated way with the wave-length employed. Steel shows no less than three maxima. The lowest permeability found for nickel was 8.5 and the highest 18.2 for wave-lengths of 54 and 585 m., respectively. For the sample of steel used the corresponding values are 32.5 and 72 for wave-lengths of 54 and 187 m. "The variation of the permeability with wave-length indicates the presence of a selective absorption or magnetic conductivity."

G. F. S.

Pilot Balloon Work. (Clip Sheet, U. S. Department of Agriculture, No. 274.)—Pilot balloon observations are now conducted by the Weather Bureau of the United States Department of Agriculture at one additional station at Memphis, Tennessee. They are telegraphed to Chicago and Washington. Original records of the observations are later mailed to the central office for reduction and study.

The eastern half of the country is fairly well covered, with the addition of this station and with those operated by the Army and Navy. West of the Great Plains, however, there is an extensive area almost entirely without free air data.

Through coöperation with authorities of the Dutch West Indies, pilot balloon observations are being made at Curacao during the hurricane season. It is possible that arrangements can be made later to have them taken throughout the year. Much of the instrumental equipment has been furnished by the Weather Bureau, which receives in return data by radio or cable. These observations, with those at

San Juan and Key West, furnish information of value in connection with the formation and movement of hurricanes.

Another example of mutually helpful coöperation in pilot balloon work is the furnishing of equipment, through the department of terrestrial magnetism of the Carnegie Institution, to the Apia Observatory, Samoan Islands. In this case also copies of the observations are forwarded to the Weather Bureau for study. R.

Kilauea Volcano Observatory. (Clip Sheet U. S. Department of Agriculture No. 278, October 22, 1923.)—A field of activity of the Weather Bureau of the United States Department of Agriculture that is but little known is the volcano investigations conducted on the island of Hawaii under Dr. T. A. Jaggar, Jr. The permanent scientific staff consists of a volcanologist, a seismologist, and a chemist. Occasionally chemists, geologists, seismologists, and physicists, both from the United States and from foreign countries, spend from a few weeks to several months at the Volcano Observatory.

The observatory is situated about 4000 feet above sea level on the brink of Kilauea Volcano, which is continually active, with a lake of molten lava. Studies are made not only of that volcano but also of Mauna Loa, nearly 10,000 feet higher, which erupts every five or six years. The eruptions of the two volcanoes are not explosive but take the form of a rather quiet extrusion of molten lava.

The routine of the station consists in daily observation and photography of the fire pit, frequent surveys to determine the height of the lava, care of several seismographs, and interpretation of seismograms. The seismograms give the distance and direction of earthquakes—five or six occur each week—and indicate the amount of tumescence or subsidence of the entire mountain top. From these seismographic data forecasts of volcanic activity from two or three hours to several days in advance are often made.

The Measurement of Thermal Conductivity. E. GRIFFITHS and G. W. C. KAYE. (*Proc. Royal Soc.*, A 724.)—A knowledge of thermal conductivity is essential in the designing of electrical machinery and of refrigerating and heating plants. For the measurement of this physical constant in substances of low conductivity, these two workers in the National Physical Laboratory have devised three pieces of apparatus with the especial purpose of economizing both time and effort. Against the face of a copper block heated electrically is put a thin plate of the substance under investigation. Heat from the copper flows through the plate into a second copper block kept cool by a stream of water circulating about it in a copper worm. The heat developed in the coil warming the first block is calculated from the resistance and the current strength. The heat removed through the worm is got by the method of the continuous flow calorimeter. One would surely expect the former of the two authors to employ

the results of his valuable experience in this method. Thus the heat supplied to the plate, as well as the heat given up by it, were measured, a check on accuracy being thereby furnished. "With proper precautions the agreement reached 1 per cent. or less." One apparatus was made for slightly compressible materials, such as pasteboard and hard wood, easily procurable in discs 45 mm. in diameter and from .5 to 4 mm. in thickness. The degree of excellence in the contact between the test material and the copper blocks was examined by varying the pressure and measuring the coefficient of conductivity. Changing the pressure from 23.2 to 61.1 pounds per square inch made no certain difference. Indeed an increase of pressure sometimes made the coefficient greater and sometimes less, thus indicating that the contact was not a factor in the measurement. "Probably the most searching test that can be applied to the apparatus, particularly as regards the thermal contact at the bounding surfaces, is the comparison of results obtained when samples of the same material in different thicknesses are tested." This test was made with three specimens of walnut. The thicknesses were .06, .09 and .15 cm., respectively. The corresponding coefficients came out .000326, .000328 and .000324 in c.g.s. units.

Apparatus No. 2 "was designed primarily for those materials of which the contact resistance at the hot and cold plates is high and for which the use of amalgamated plates becomes necessary. The same apparatus proved also to be convenient for the study of variation from point to point in the conductivity over the area of a large sheet of material, such as ebonite or micanite." For the amalgamation to assure good contact, it was found that the plates must be fairly flat. Of course a correction was applied for the fall of temperature through the mercury film.

Apparatus No. 3 was for materials obtainable in thin layers only, so that a considerable quantity of heat traversed the layers and had to be provided by the heating coil.

The effect of moisture content on conductivity was investigated in the case of spruce. As the content rose from 3.4 per cent. to 17.0 per cent. the conductivity rose linearly from .000292 to .000340.

The coarser the grain of wood, *i.e.*, the fewer the annual rings per inch, the smaller is the conductivity. The conductivity parallel to the grain is about twice that perpendicular to the grain and either radial or tangential to the rings. The radial conductivity is about 5 or 10 per cent. larger than the tangential, since in travelling tangentially the heat meets the interstices between the fibres as well as the medullary rays, whereas the rays do not interfere with the passage of the heat radially.

Silk fabric, rice paper and Balsa wood all have a coefficient of approximately .0001. No other wood showed as small a value as the last named, which has a density of only 6 or 9 pounds per cubic foot.

G. F. S.

The Thermal Conductivities of Metal Crystals—I. Bismuth. G. W. C. KAYE and J. K. ROBERTS. (*Proc. Royal Soc.*, A 724.)—Hitherto all the measurements of the thermal conductivity of metals have been made upon pieces of metal containing the crystals in random arrangement. The purpose of this investigation is to determine the conductivity of a metallic crystal in different directions with regard to the crystalline axis and to compare the values thus obtained with the conductivity of an ordinary piece of the same metal. Bismuth was chosen because large crystals can be grown and because it does not crystallize in the cubic system.

Parallel to the trigonal axis the conductivity was found to be in c.g.s. units .0159. Perpendicular to the axis it is .0221. The ratio of the conductivities is 1.39. This ratio had been measured by others and ranged from 1.37 to 1.49.

On the assumption that ordinary bismuth is a conglomerate of small crystals, its conductivity should be .0195. Jaeger and Diesselhorst have obtained by measurement the value .0193, which is sufficiently near to the computed value. G. F. S.

The Sensitivity of the Ear as a Function of Pitch. F. W. KRANZ. (*Phys. Rev.*, July, 1923.)—"The sensitivity of the ear can best be expressed in terms of the minimum sound intensity which is audible." The source of sound was a thermophone. In this the alternating current from a vacuum tube oscillator flows through a platinum strip supported in the case of a telephone receiver held firmly against the observer's ear. The periodic changes of temperature in the metal cause corresponding changes in the pressure of the confined air, from which the sensation of sound arises.

By varying the inductance and capacity of the oscillating circuit it was possible to get a range of frequencies from 360 to 3000 per second. The procedure was the following: The intensity was fixed at so small an amount that it was insufficient to produce even the least sound at any frequency. The intensity was then doubled and kept constant while the range of frequencies was run through. At certain frequencies the constant intensity barely produced the sensation of sound. These frequencies were noted. The intensity was thereupon doubled and again the range of frequencies was tried. At frequencies different from those previously noted sound was heard. The increase in intensity was made a sufficient number of times.

Thirty normal ears were examined. In one instance a certain intensity was just great enough to be audible at no less than seven frequencies or pitches. It was quite common to find five such frequencies. The right and the left ears of the same person are not alike and the difference is at times astonishingly great. In one particular case one ear required at a frequency of 1600 per second about 100 times as much intensity for audibility as did the other ear. In still another ear lowering the frequency by 80 cycles, little more than

a semitone in the part of the scale concerned caused the sensitivity to become 200 times as great.

From person to person the curves connecting intensity and sensitivity vary to such an extent that it would seem that they might be used, as are the Bertillon prints, for purposes of identification, were it not necessary to have the untrammelled judgment of the observer in order to form the curve. From the average results of the thirty ears examined, it is evident that the sensitivity increases from a frequency of 360 up to that of 1500. Over the range from 1500 to 3000 there is little change.

G. F. S.

A New Method of Getting Residual Rays (Reststrahlen).

M. CZERNY. (*Zcit. f. Phys.*, Vol. 16, July, 1923.)—In 1896 Rubens and E. F. Nichols published a method of separating from the entire complex of infra-red radiation a limited range of wave-lengths, the residual rays. This consisted in causing the complex to be reflected in turn from a series of polished, flat plates of a non-metallic substance such as rock salt that shows in the infra-red a marked metallic reflection. Those wave-lengths for which the reflector acts as a polished metal emerge from the last reflection but little weakened, while the other wave-lengths, for which the reflecting plates are transparent, come out materially reduced in strength. A drawback of the method lies in the need of finding a different reflector for each particular group of wave-lengths and, further, of getting from three to five large plates of it polished.

The ordinary sources of radiation for work in the infra-red emit very little energy in waves shorter than .0005 mm. By far the largest quantity of energy is given off in waves whose lengths range from .0005 to .012 mm. (radiation of short wave-length). It is the gamut of waves extending from the last up to those about a dozen times as long, from wave-length .012 mm. to .150 mm., for which the residual ray method is especially applicable. For this range there is considerable energy present, but it falls off rapidly with increasing length of wave. There is only a little energy in all the waves together whose lengths exceed .150 mm. The problem of segregating the residual rays depends upon discovering some way of reflecting the infra-red radiation in such a manner that the radiation of short wave-length be enormously reduced, while at the same time the residual rays are not greatly weakened. The author finds his solution in following a suggestion made by Rubens that the angle of polarization be employed. First, the complex of infra-red radiation is plane polarized by reflection at the proper angle from selenium mirrors. The reflected light then falls on a plane mirror of a substance having metallic reflection of the residual rays. The angle of incidence is determined by calculation so that there shall be no reflection at all of the plane polarized light whose wave-length places it in the middle of the radiation of short wave-length. Thus the reflected light is weak in wave-lengths both longer and shorter than the one that is extinguished, but retains

in considerable strength the longer wave-lengths that are metallically reflected. In spite of the loss they have suffered in becoming plane polarized the residual rays come out of the new process approximately as strong as in the former method. This loss is avoidable by the use of rock salt or fluorspar instead of the selenium plate. Selenium is largely free of dispersion and consequently plane polarizes a wide range of wave-lengths, while the other substances mentioned reflect the infra-red radiation with the short wave-lengths polarized and with the long waves of residual radiation not polarized. When this mixture of light in different conditions falls on the second plate at the proper angle, it is still the short waves that are extinguished. The residual rays are reflected without being polarized.

The fundamental idea of the method is, as has been said, due to Rubens, and according to the author is "probably the last suggestion made by him in the long series of methods which he devised for the isolation of infra-red waves." He died in July, 1922. G. F. S.

In Crystals is Sliding Friction Independent of the Pressure Normal to the Surfaces? M. POLANYI and E. SCHMIDT. (*Zeit. f. Phys.*, Vol. 16, July, 1923.)—Inside of a steel cylinder a weight was supported on bearings so that it would move parallel to the axis of the cylinder, when this was tilted. From the weight a rod ran to the end of a wire firmly supported at the other end. When the cylinder was tilted, the weight pulled on the wire and tended to stretch it. The wire was a single crystal of tin or of zinc produced by Czochralski's method. The yielding of the wire took place along planes determined by its crystallographic constants. Did the force required to make one plane slide over its neighbor depend on the pressure at the planes? To find the answer the cylinder was inclined until the wire, seen through a protected window, just began to lengthen. It was at once replaced in its first position, the pressure within was raised by means of a CO₂ cylinder and the experiment was repeated. It was impossible to find any difference of angle caused by a change of the pressure from 1 to 40 atmospheres, and yet in the latter case the surfaces must have been pressed together with forty times as much force as in the former, since the pressure within the cylinder was applied equally in all directions. G. F. S.



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THE POLARIMETER AND ITS PRACTICAL APPLICATIONS.*

BY

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I. INTRODUCTORY.

INSTRUMENTS used for the measurement of polarized light are variously called *polariscopes*, *polarimeters*, and *elliptic analyzers*. The first two designations are common when they measure the azimuth of a rectilinear vibration, and the last when they determine the ratio of the axes—the “ellipticity”—of an elliptic vibration. In the present article, the designation *general polarimeter* is applied to those instruments which furnish a complete specification of the polarized light measured, namely, both azimuth and ratio of axes. Where it is desirable to distinguish between them, they are designated as *azimuth polarimeters*, *elliptic polarimeters* or *general polarimeters*, as the case may be. By so doing, it is hoped to stress with benefit the unity of principle of the different types. As to *practical application* this is meant to include the purely scientific, as well as the industrial applications. The sugar chemist employs an azimuth polarimeter for grading factory products, a practical application which is also industrial. The petrologist may use a polarimeter to identify crystals as a purely scientific application, nevertheless, the application is practical, although it may not be industrial.

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II. FUNDAMENTAL FACTS AND RELATIONS.

1. *Vibration of Light*.—For purposes of analysis, light is considered to be a homogeneous wave-train which may be described as subjecting a vibrant electrical particle of the medium traversed, to a pendular vibration in the tangent plane to the wave-front. This vibration is constant in frequency with both time and azimuth (direction in the tangent plane), and constant in amplitude with time, but in general variable with azimuth. Dependent upon the facts to be explained, this wave-train is assumed to be made up either of two mutually perpendicular rectilinear vibrations having the same frequency but in general differing in amplitude and phase; or of two opposite circularly vibrating trains having the same frequency but also differing, in general, in amplitude and phase. Both of these concepts require the vibrant particle to travel in a definite elliptical path having a definite azimuth and definite frequency. This picture seems, at first thought, far removed from a real description of light waves. Light reaching any point in space from a source homogeneous as to frequency must be a composite of myriads of elementary elliptically vibrating wavelets, each being the result of an electron of a given atom recovering from a shock received through a chance collision, we will say, with another electron, and each ceasing to radiate after the supply of energy received in that shock is spent. We should expect, therefore, the ellipticities of the elementary vibrations to be distributed by pure chance between a circle traced in one direction and a circle traced in the opposite direction, and the azimuths of these ellipses to be uniformly distributed in all directions in the plane tangent to the wave-front. From interference experiments, however, we know that the elementary wave-trains have, on the average, upwards of a million waves; that is, the form of vibration of each remains the same for upwards of a million vibrations. It follows that the myriads of elementary radiators in a homogeneous source must combine in their effect at any point to produce a vibration there whose form diverges from an ellipse less than does that of the planet of Mercury. In spite of this relative constancy, however, experiments to detect form of vibration in natural light have been in vain, owing to the extremely short time intervals involved (10^{-9} second). Hence, although we are convinced that natural light furnishes at any given moment vibrations of a definite elliptical form, that form is not sufficiently enduring to serve to reveal the

truth of the conclusion, much less to serve as a practical light source of definite vibration form. The method of obtaining a definite and enduring elliptical vibration is to first sift out of natural light rectilinear vibrations of definite azimuth and then, by chosen devices, convert these into the desired elliptical form.

2. *Propagation of Light*.—Various crystalline media, isotropic media subjected to magnetic electric or mechanical stress, and a very large number of liquids possessing an asymmetric carbon atom effect a surprising though simple change in the vibration of the light which they transmit. The explanation of the phenomena is based on the observation that these media possess the remarkable property of transmitting waves of certain vibration characteristics faster than others.¹ By virtue of this property, a wave-train entering such a medium is separated into two component wave-trains, one of which outdistances the other. By choosing conditions so that these two waves are differently refracted, they may be entirely separated. Or in case they are not differently refracted, they will, on emerging into an isotropic medium, combine to form a single wave-train whose ellipticity and azimuth are in general different from that of the entrant train.

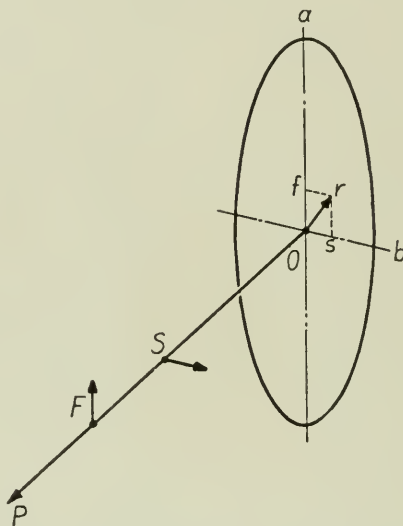
These media fall into two general classes according to the vibration form which they transmit. The first class, known as *plane doubly refracting* media, separates the incident light into two rectilinearly vibrating wave-trains whose vibrations are mutually perpendicular. In “uni-axial” crystals, one of these vibrations, known as the ordinary ray, is transmitted with the same velocity in all directions through the crystal; the other, known as the extraordinary ray, is transmitted with a velocity which in general varies with the direction. In one direction, designated as the *optic axis* of the crystal, the ordinary and extraordinary rays are propagated with equal velocity. In “bi-axial” crystals, there are two equal velocity directions, both rays being extraordinary in that the velocity of both varies in general with the direction. Calcite, mica, a number of liquids normal to the lines of force in an electric or magnetic field, glass under tension or compression, are important examples of this class. The second class is *circular doubly refracting*. It transmits light in the form of two circular vibrations—one whirling around the direction of propagation clockwise, the other counter-

¹ The analogous effects arising from a difference in the absorption of the two components are not treated in this article.

clockwise. Quartz along the optic axis, sugar solutions and liquids generally having an asymmetric carbon atom and substances along the lines of force of a magnetic field, are examples of this class.

3. *Review of Mechanical Theory of Propagation of Elastic Waves.*—While it would be impossible to give, within the scope of an article such as this, even a brief theory of crystal optics, an outline of the fundamental assumptions and conclusions may not be superfluous. Fresnel's mechanical theory of light trans-

FIG. 1.



Shows a single displacement (Or) propagated in an elastic medium as two separate displacements (F and S) respectively parallel to the axes (Oa, Ob) of the rigidity ellipse in the plane of which the original displacement lies.

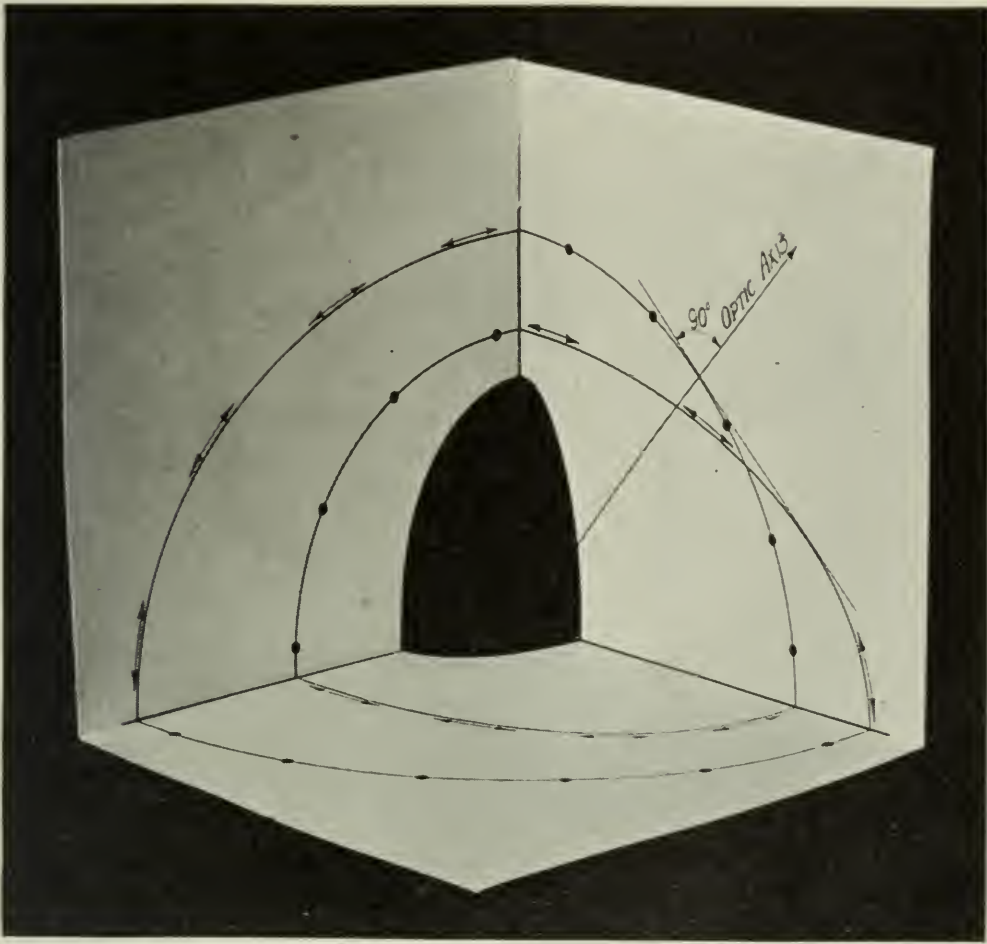
mission gives a relatively simple framework in which the main facts may be coördinated.

Every elastic medium has its "ellipsoid of elasticity," whose semi-axes represent, respectively, the displacements of a particle from its position of rest relative to its neighbors when subjected to a given force in those directions. Every diametral section of that ellipsoid is an ellipse whose semi-axes represent likewise the displacement produced by the same force in their respective directions. For simplicity, we shall use here the corresponding *rigidity ellipsoid* which represents the force of restitution for a given displacement—the velocity of propagation of an elastic displacement through any medium being directly proportional to the square root of its rigidity.

In Fig. 1, Oab is a diametral section of the *ellipsoid of rigidity* normal to the direction OP of propagation of a transverse dis-

placement Or . The component displacement Of , parallel to the major axis of the ellipse, is propagated along OP with a velocity proportional to the square root of the semi-major axis Oa ; that parallel to the minor axis is propagated along the same direction

FIG. 2.



Quadrant traces of the ellipsoid of rigidity (in black) and the consequent wave-front traces on the coordinate planes for displacements respectively parallel and perpendicular to the coordinate planes. Displacements perpendicular to the given plane marked by dots; parallel, by double arrows. The medium is bi-axial.

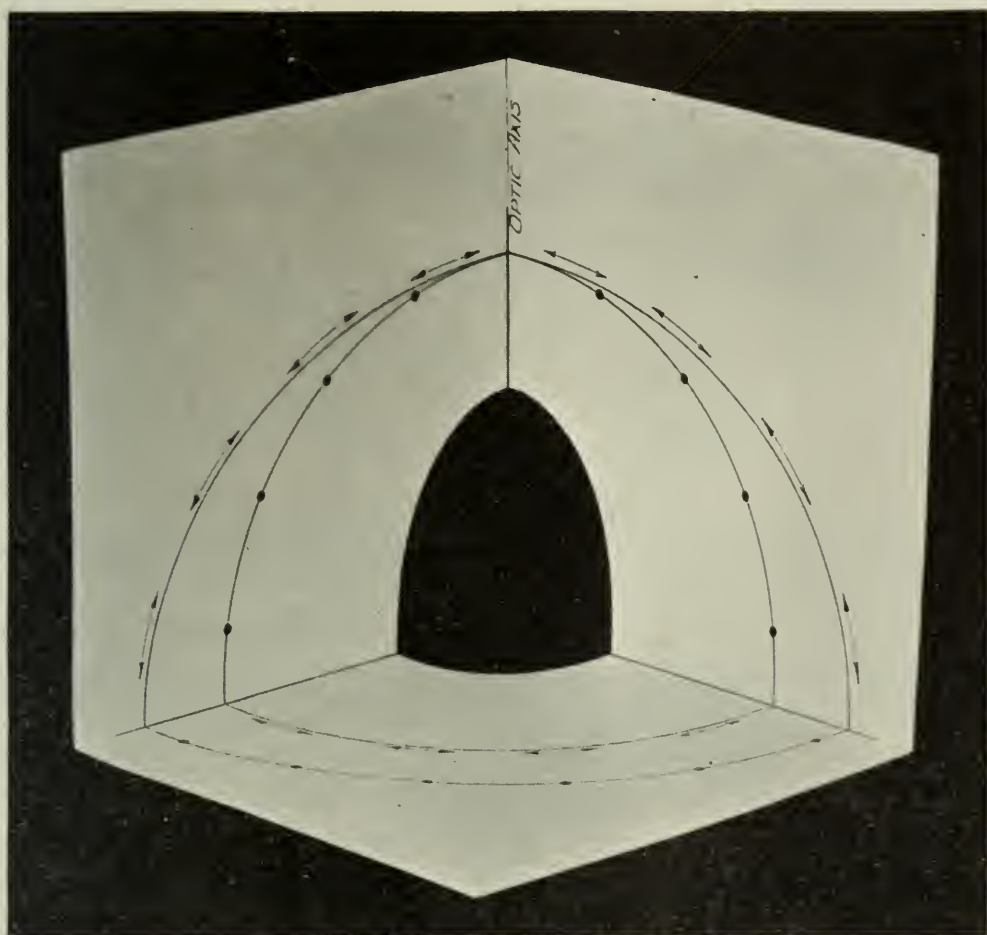
with a velocity proportional to the square root of the semi-minor axis Ob . After a given interval, the faster component will have reached F , while the slower has only reached S . Thus any transverse vibration in the plane Oab will be propagated along the direction OP as two separate rectilinearly vibrating wave-trains whose planes of vibrations are parallel, respectively, to the major and minor axes of the elliptical section of the ellipsoid of rigidity, whose plane is normal to the direction of propagation. The gen-

eral case of radiation in all directions from a point in an elastic medium is illustrated by Fig. 2, which gives quadrant traces of the two wave-fronts on each of the coördinate planes, the coördinate axes being the semi-axes extended of the ellipsoid of rigidity—shown in black. Vibrations parallel to the major axis of the rigidity ellipsoid (vertical coördinate axis) should obviously be propagated throughout the horizontal coördinate plane with a constant maximum velocity, hence the trace of this wave-front on that plane is circular—marked with dots. Similarly, vibrations parallel to the intermediate and minor axes of the ellipsoid of rigidity have respectively circular traces on the right and on the left vertical coördinate planes—their respective radii representing intermediate and minimum velocities. The vibrations of these three circular traces are all perpendicular to the respective coördinate planes. The wave-front traces of the vibrations parallel to the coördinate planes, indicated by the double arrows, must obviously coincide on the coördinate axes with the like directed vibrations of the circular traces just described, hence their velocity must vary with their direction of propagation in the plane. Theory shows that these traces are elliptical, the axes of the ellipse coinciding with the axes of the rigidity ellipsoid. For directions of propagation lying outside these *principal sections* of the ellipsoid of rigidity the effect may be visualized by imagining Fig. 1 superposed on Fig. 2 with O of 1, at the origin of 2, and OP given the desired direction. The ellipse Oab being a diametral section of the rigidity ellipsoid whose normal is OP , determines the direction of vibration in the fast and slow wave-fronts as also their velocity of propagation.

From Fig. 1, it is seen that if the rigidity ellipse becomes a circle, the two component vibrations are propagated along OP with equal velocity, hence all components are; as a result, the two wave-trains merge into one. Since there are in general two circular diametral sections of an ellipsoid *and only two*, there should be two directions relative to the rigidity ellipsoid in which the two wave-fronts coincide in their velocity and only two. One of these directions is indicated in Fig. 2 by the intersection of the two wave-front traces in the right vertical plane. The other direction is given by the symmetrically placed point in the second quadrant of the same plane. When dealing with an elastic electrical medium—optical medium—the direction of this intersection from the origin is called the direction of *equal ray velocity*. Since

the velocity of the wave-front is measured along the wave normal, that is, by the perpendicular distance between successive positions of the wave-front, the normal to the tangent plane common to the two wave surfaces at this point gives the direction of *single wave velocity* or the *optic axis*. In general then, a medium possesses

FIG. 3.



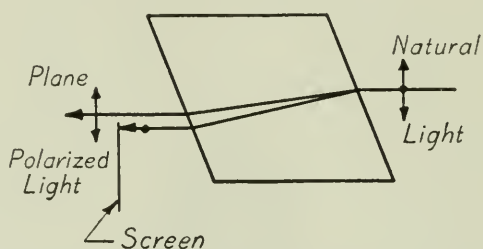
A special case of Fig. 2 where the rigidity ellipsoid (in black) is a figure of revolution, consequently the medium is uni-axial.

two optic axes and only two. When the rigidity ellipsoid is a spheroid, it has but one diametral section which is circular, hence only one direction of equal ray velocity and this coincides with the direction of the single optic axis. Fig. 3 shows the wave-front traces on the coördinate planes for such a medium—the two crossing points in the first and second quadrants of the vertical plane of Fig. 2 merging here into one contact point on the vertical axis—axis of the spheroid. When the ellipsoid of rigidity is a

sphere, all directions are, of course, equal velocity directions, the medium is *optically isotropic*.

Returning to the general case illustrated by Fig. 2, it may be stated that the directions of vibration in the two wave-fronts are determined by the angles which the direction of propagation makes with the two optic axes. From geometrical considerations, it may be shown that *the directions of the component vibrations occupy middle positions between the two planes containing each an optic axis and the wave normal*. Applying this rule to uniaxial media, these two planes merge into a single one, hence the two vibrations lie respectively in and perpendicular to the plane of the optic axis and the wave normal. In the immediate vicinity

FIG. 4.



Application of a plane doubly refracting substance to sift plane polarized light out of natural light. The rhomb causes a larger lateral displacement of the more refrangible component (vibration perpendicular to the plane of the paper) and this is intercepted by a screen.

of an optic axis of bi-axial crystals, this rule requires the direction of vibration in both outer and inner wave-fronts to rotate in the plane of the wave-front in going around the optic axis, and just half as fast. Thus, as seen from Fig. 2, in passing 180° around an optic axis the vibration in its immediate vicinity, on both the outer and inner wave surfaces, changes in direction by 90° .

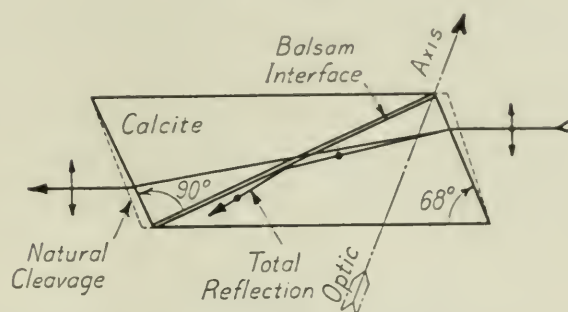
For the large class of substances which propagate light in the form of two opposite circular vibrations differing in their velocity of transmission, a simple mechanical theory is lacking. We shall accept the fact without attempting to explain it and follow it later to a simple conclusion.

III. POLARIZERS AND ANALYZERS.

The single wave-train of an isotropic medium is, in general, separated on entering a medium whose ellipsoid of rigidity is not a sphere, into two differently refracted rectilinearly vibrating wave-trains, one of which under certain conditions may be diaphragmed off. Thus a device is furnished for sifting "plane polarized" light out of "natural" light, as illustrated in Fig. 4.

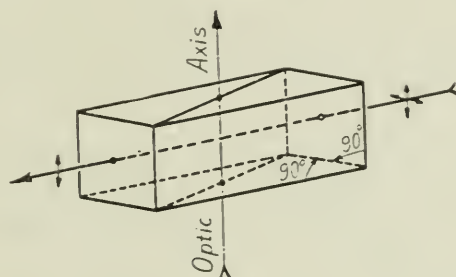
Polarizers of this type were in early use and still are used to a certain extent. The most common polarizing device, however, is the so-called *Nicol prism* (named after its originator, William

FIG. 5a.



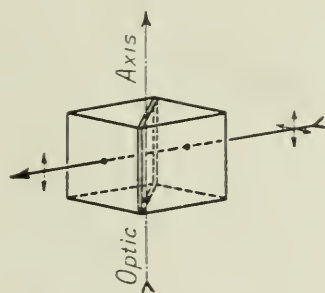
Nicol prism. The component vibration parallel to the interface is totally reflected, the transmitted vibration being parallel to the short diagonal of the end face. The rays are laterally displaced. Aperture of polarized cone, 29° .

FIG. 5b.



Glan-Thompson polarizer. No lateral displacement of rays. Aperture of polarized cone varies with slope and composition of interface, e.g., with Canada balsam, 27° ; with linseed oil, 35° . Vibration of transmitted light parallel to plane of interface.

FIG. 5c.

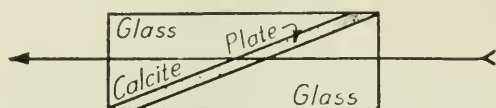


Glan polarizer. Air interface. Characterized by its extreme shortness, 0.9 of its diameter. Aperture of polarized cone nearly 8° . Multiple reflections at interface disturbing. Vibration of transmitted light parallel to plane of interface.

Nicol) illustrated in Fig. 5a. The light enters the sloping end face of a parallelopiped of Iceland spar, a uni-axial medium, fashioned from the natural rhomb as indicated. Here the two component wave-trains are differently refracted, after which the more refrangible is totally reflected at an interface of Canada

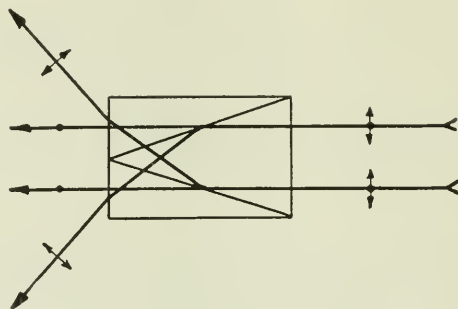
balsam, linseed oil or other suitable material, interposed at the right slope while the less refrangible ray is transmitted with little loss and no refraction. A coat of black paint on the lateral faces of the rhomb absorbs the reflected ray. Other important polarizers of this type are illustrated in Figs. 5b and 5c. Necessary features of a satisfactory polarizer are perfect polarization and high transmission with also, for colorimetric work, neutral absorption. Other considerations of more or less importance, depending on the application, are angular size and amount of lateral displacement of the cone of polarized rays, symmetry of the same

FIG. 5d.



Feussner polarizer. This would be distinctly preferable to the preceding polarizers were it possible to obtain a cement possessing the necessary optical properties.

FIG. 5e.



Ahrens polarizer. Effectively a double Glan-Thompson polarizer in which, however, the discarded component is in part transmitted but diverted out of the regular polarized cone.

with respect to the visual axis of the prism, ratio of diameter to length of prism, amount of distortion and astigmatism. All of the Nicol type transmit the so-called extraordinary ray, for which the spar possesses a refractive index varying with the direction of the ray through the crystal; hence a theoretically perfect image through the prism is impossible for any but parallel rays because of the resulting astigmatism—a condition of importance in polarization microscopes.² By using a total reflecting plate of spar in a medium of CS_2 Jamin designed a polarizer which transmits the ordinary ray, for which the spar, as well as the CS_2 , has a refractive index independent of the direction.³ Brace used this

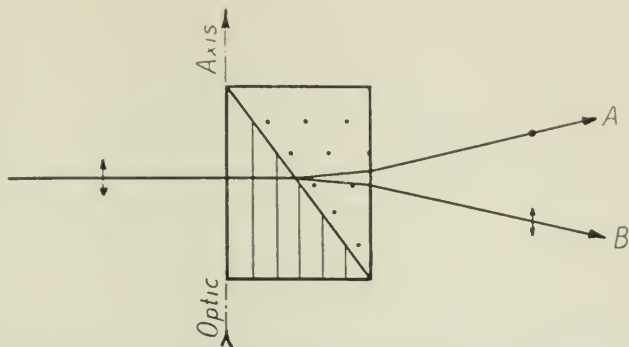
² S. Becker, *Ann. d. Physik.* [4], 47, p. 285 (1915).

³ This principle has been applied in the so-called Feussner prisms, Fig. 5d—Feussner, *Zeitschr. Instrk.*, 4, p. 41, 1884; and Schulz, *Zeitschr. Instrk.*, 40, p. 180, 1920—which are consequently free of this kind of astigmatism.

design for producing a very perfect half-shade polarizer, but it, owing to the difficulties of construction and maintenance, has found very limited use.

The need for polarizers of larger cross-section relative to their length than the ordinary design possesses, has led to a built-up type such as shown in Fig. 5*e*, which serves well for some

FIG. 6.



Wollaston polarizing prism. Consists of two equal calcite (or quartz) prisms with their optic axes at right angles to each other and to the visual axis. Incident rays are separated at the interface into plane polarized components equally and oppositely refracted. On emergence each suffers further refraction but not as customarily assumed, exactly equal. Associated with the refraction there is also dispersion, the effect of which needs to be eliminated in its applications.

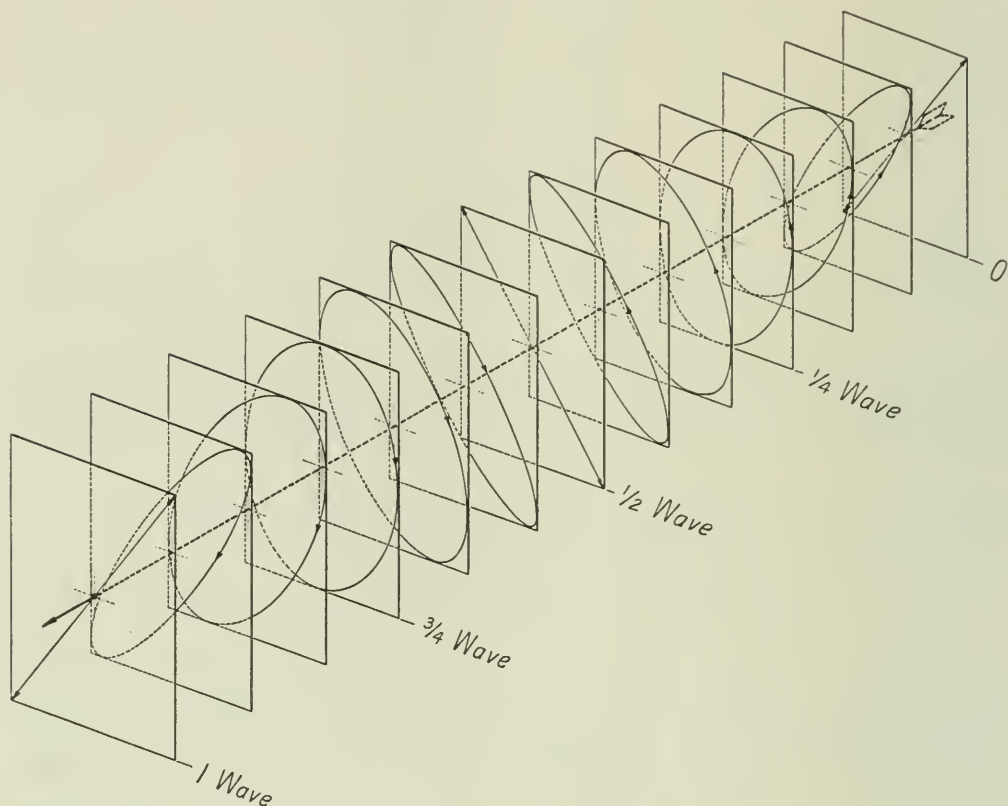
kinds of work. Another polarizer of considerable practical importance is the Wollaston prism illustrated in Fig. 6.

IV. RETARDATION PLATES AND COMPENSATORS.

For converting a rectilinear into a definite elliptical vibration, the most convenient device is a doubly refracting plate having its faces normal to one of the axes of the rigidity ellipsoid if the plate is bi-axial; or simply parallel to the optic axis, if it is uni-axial. Mica is naturally adapted for such purposes because its cleavage plane fulfills the first requirement and polishing is unnecessary. Fig. 7 illustrates the change in form of an incident rectilinear vibration as it is propagated through such a plate—equal or no absorption of the two components being assumed. The problem of determining the elliptical form of the vibration at any point is simply one of the superposition of two mutually perpendicular pendular vibrations both having the same period, each a definite amplitude and the two a definite phase difference. It is readily seen that there are two controlling factors entering into the production of a definite ellipse from the incident rectilinear vibration, namely, the thickness of the plate and its azimuth with respect

to the incident vibration—the first determining the phase difference and the latter the relative amplitudes of the component wave-trains. With an azimuth giving equal amplitudes the maximum ellipse, a circle, is produced by a plate which retards the slow wave-train a quarter wave-length behind the fast; or, three-quarters wave-length; and so on. From the figure, it is seen

FIG. 7.

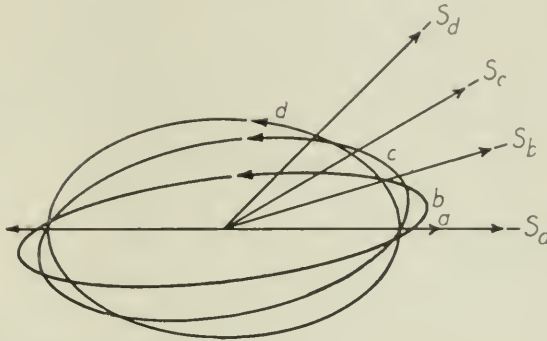


Change in form of an elliptic vibration with distance along the path when the horizontal component is propagated with a greater velocity than the vertical.

that the direction of motion in the circle is opposite in the second case to that in the first. If the *ellipticity* (ratio of axes) in the first is considered to be $+1$, it is designated as -1 in the second, so that by convention the sign of the ellipticity indicates the direction of motion of the vibrant particle in its elliptical path. By rotating the quarter-wave plate through an azimuth of 90° around the ray, the fast and slow waves are simply interchanged so that the circular vibration produced in the first position becomes, with the plate in the second position, an opposite circular vibration. By varying its azimuth, therefore, a quarter-wave plate will pro-

duce from plane polarized light any ellipticity between $+1$ and -1 . Likewise, a thicker or thinner plate will produce any ellipticity between its maximum and equal minimum as illustrated by Fig. 8. Both the variable-thickness and variable-azimuth methods of

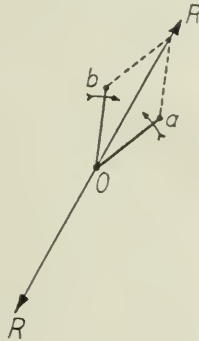
FIG. 8.



Plane polarized incident light vibrating parallel to S_a , on traversing a doubly refracting plate of order less than a quarter-wave, emerges unchanged for an azimuth S_a of the plate; and as the respective elliptic vibrations b, c, d for azimuths S_b, S_c, S_d of the plate. With S_d at 45° (as drawn) to the incident vibration the ellipticity of d is a maximum. With plate azimuths at 90° to those given the paths are unchanged, merely traced by the vibrant particles moving in the reverse direction.

producing a given ellipticity are in common use. It is obvious that a second equal plate at an azimuth of 90° to a first will neutralize any ellipticity produced by the first, hence the same device used for producing a given elliptical vibration will serve

FIG. 9.



A vibrant particle simultaneously subjected to two equal period but oppositely rotating circular displacements (Oa and Ob) traces a rectilinear path (RR) when the two amplitudes are equal. When the amplitudes are unequal the path is an ellipse traced in the direction of motion of the component having the larger amplitude.

to "restore" such a vibration. Such *compensators* are in general use for measuring the constants of polarized light. A quarter-wave plate can be adjusted in azimuth so as to restore an ellipticity of any magnitude from $+1$ to -1 ; a plate less or greater than

a quarter-wave may be so placed in azimuth that it will restore any ellipticity between the maximum and equal minimum magnitudes it will produce from plane polarized light.

Two opposite circular vibrations of equal amplitude combine, as illustrated in Fig. 9, to produce a rectilinear vibration of double amplitude; or, *vice versa*, a rectilinear vibration will be propagated as two opposite circular vibrations in media that transmit only circular vibrations. Where these two wave-trains are propagated with different velocities, they may be isolated, in the same way as rectilinear vibrations, by diaphragming or by total reflection, if conditions exist for a difference in refraction. Our interest here is, however, confined to what happens when the two wave-trains are propagated over the same path with merely a difference in velocity. Since, as seen from the figure, a change in relative phase of the two vibrations merely shifts the direction of the resultant rectilinear path, we have in that case a simple rotation of the plane of polarization whose magnitude is proportional to the thickness of the rotating medium traversed. Plates of "right" and "left" rotatory quartz (faces perpendicular to the optic axis) are commonly used as compensators to restore the azimuth of a rotated rectilinear vibration.

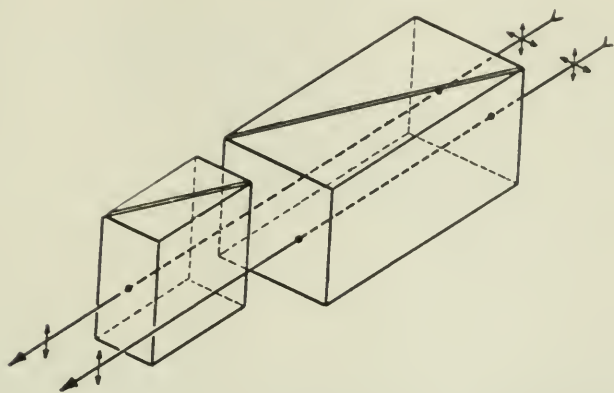
V. AZIMUTH POLARIMETERS.

For precision measurement, the brightness half-shade method is in dominant use. In this, the criterion for a setting is a brightness match of usually two, but sometimes three, contiguous parts of the field of view. This half-shade field is obtained by polarizing the light at two slightly different azimuths in the respective parts to be matched, by using either a Cornu-Jellett "split Nicol" or a Lippich combination of one Nicol covering the whole field followed by a second at a slightly different azimuth covering a part only (Fig. 10). The Cornu-Jellett Nicol (Fig. 11) is in principle a common Nicol from which has been removed a thin, wedge-shaped, central longitudinal section perpendicular to the interface, and the remaining parts closed together, thus furnishing in the respective parts of the field rectilinear vibrations of slightly different azimuth. The Lippich system has the advantage of readily changing the difference in the two azimuths—which changes the brightness and sensibility in opposite directions—but introduces asymmetry in that the second Nicol reduces

the brightness of its half of the field below that of the other. In dealing with purely azimuth measurements, however, this effect is readily eliminated, but not so when ellipticities are involved.

With either of these half-shade polarizers and a monochromatic light source, a setting is made by rotating the analyzing Nicol to a match near the extinction azimuth. It is important to note that the sensibility of this kind of a half-shade is double that of an ordinary photometric field where, in making a setting, the light intensity is varied in one half only. Here, shifting the

FIG. 10.



Lippich half-shade polarizer. By rotating the larger Nicol about the visual axis the azimuth of vibration in the right half of the field is varied at will, while the left half is only changed in amplitude, not in azimuth. By such adjustment the brightness level of the field matched by an analyzing Nicol is readily varied. (Used as an analyzer, the direction of the light is reversed.)

azimuth of the analyzing Nicol from a true setting reduces the intensity of the one part at the same rate that it increases it on the other.

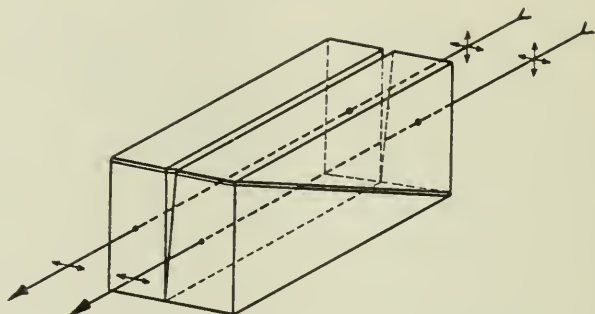
With a heterochromatic source (commonly some definite "White Light" through a specified filter) the dispersive power present in all rotatory substances necessitates the employment of an oppositely rotatory compensator of practically equal dispersing power of the substance under investigation and whose thickness can be varied to compensate for the rotation of the substance. A common form consists of a wedge combination of right and left rotating quartz which compensates rotation in either direction.

Both the rotation and the fixed analyzer types have been brought to such a high state of perfection that under the best conditions careful observers will differ in their determinations by not more than two or three thousandths of a circular degree.

VI. APPLICATIONS OF THE AZIMUTH POLARIMETER.

1. *Saccharimetry*.—By far the most important and most common application of the azimuth polarimeter is in grading the products of the sugar factory for which work it is indispensable. There are upwards of 100 sugars known and nearly all of these in solution rotate the azimuth of a rectilinear vibration in one direction or the other. Commercial sugars are bought and sold and the import duties collected upon tests by this instrument. The simple proportionality between solution concentration and optical

FIG. 11.



Cornu-Jellett half-shade Nicol, showing section removed, after which the parts are closed together giving slightly different azimuths of vibration in the two halves of the field. This design serves equally well as polarizer or analyzer. The more common construction, in which only one of the two parts has a wedge removed, will serve equally well as an analyzer, but introduces ellipticity when used as a polarizer.

rotation, the extreme simplicity of the manipulation, the high precision in measurement and the reliability of the interpretation makes the application so important as to render the situation very serious for the sugar industry as also for the Government laboratory when, as during the war, the possible supply and repair of these instruments is cut off.⁴

2. *Photometry*.—In photometry, and incidentally in optical pyrometry, the principle of the azimuth polarimeter is applied in a unique way. It is obvious that, viewed in the direction of the arrow through the Wollaston prism of Fig. 6, the two separate fields in the respective directions of *A* and *B* would appear superposed. By limiting their extent and increasing at the same time their angular position, they may be separated more or less. By employing a device which at the same time eliminates overlapping,

⁴ Had the Bureau of Standards not undertaken the repair of polarimeters at one time when the foreign makers were inaccessible and our own optical manufacturers unable to do so, it is difficult to estimate what would have been the consequences of the resultant paralysis to the industry.

they may be juxtaposed under desired conditions. The light from the two respective fields is rectilinearly polarized at right angles so that by interposing a simple Nicol and varying its azimuth a match of the two may be produced. The match azimuth of the analyzing Nicol serves to determine the relative brightness of the two given rectilinear vibrations in the respective sources and of course the relative brightness of the two sources in case they are unpolarized. When the light is partially polarized an additional setting made with the instrument rotated in azimuth through 180° will obviously give the total brightness ratio. This principle was first used by Koenig in his spectrophotometer; is used in the Koenig-Martens spectrophotometer,⁵ an improvement on the Koenig, and in the Martens photometer,⁶ schematically illustrated by Fig. 12, in which are omitted the lenses and diaphragms necessary to a satisfactory realization of the design. In the spectrophotometer, the light passes through a dispersing prism before entering the Wollaston of Fig. 12, and the windows at *A* and *B* are respective parts of a single slit.⁷

3. *Colorimetry. The Arons Chromoscope.*⁸—In this instrument (Fig. 13) the principle of the azimuth polarimeter is applied to obtain various colors by the selective transmission of "white light." Its range of color production, relative simplicity and independent reproducibility give it a unique position among colorimeters. It is almost universal, failing only to furnish the very pure colors, notably in the red. All mixed colors are reproducible

⁵ *Ann. der Physik.* [4], 12, p. 984 (1903).

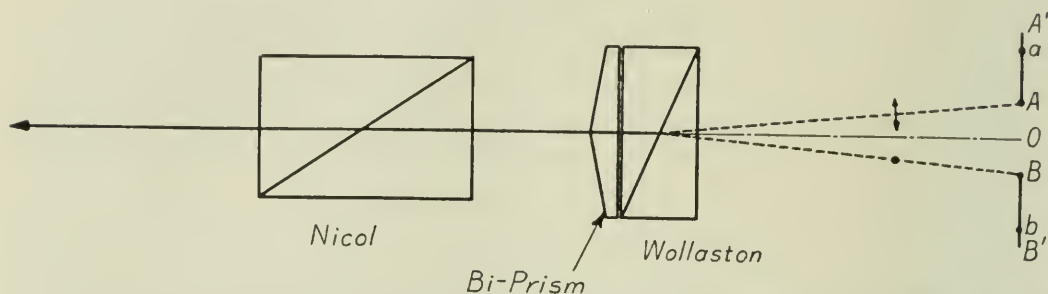
⁶ *Physik. Zeitschr.*, 1, p. 299 (1899).

⁷ The Colorimetry Section of the Bureau of Standards has compared their Koenig-Martens spectrophotometer with the known transmission of a rotating sector and drawn therefrom the following conclusions: (1) The probable error of a single observation in the brightest part of the spectrum is about 0.007 of the transmission; (2) the probable error of a single observation is about 0.01 of the transmission (for a transmission of 0.37) for homogeneous light ranging from $\lambda_{Hg} = 435.8$ millimicrons to $\lambda_{He} = 706.5$; (3) the actual error of the mean of ten observations is usually less than 0.01 of the transmission for the range $\lambda = 430$ to $\lambda = 700$, for transmissions as small as 0.1. The Optical Instruments Section has compared their Martens photometer, which is used for measuring the transmission of optical glass and optical instruments, with a rotating sector, and found that, based on the average of ten sets of readings each, the error made by three observers in measuring a known transmission of .80 ranged from zero to .005.

⁸ L. Arons, *Ann. der Physik.* [4], 39, p. 545 (1912).

beyond one's power of discrimination. The simpler form of the instrument consists of a variable thickness of rotatory quartz placed between two Nicol prisms, the analyzing Nicol being mounted in a graduated circle. Viewing a source of "white

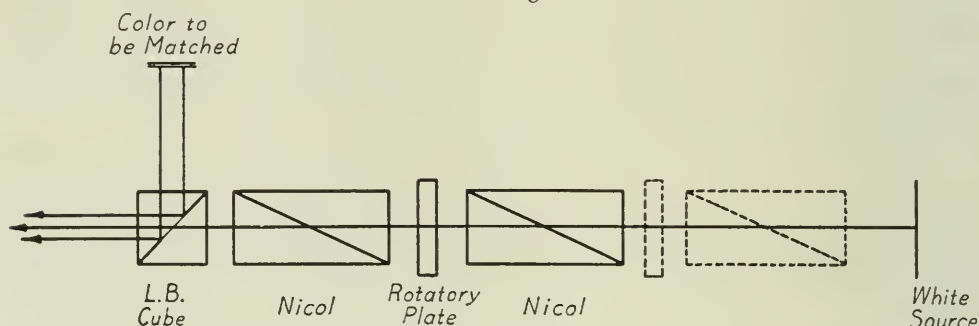
FIG. 12.



Polarization and half-shade elements of the Martens photometer. The Wollaston prism directs to the eye from the field AA' only the vertical components of the light vibrations, and from BB' only the horizontal. The bi-prism brings the two fields into contiguity without overlapping. The Nicol is rotated to a brightness match, its setting giving a measure of the relative brightness of the two fields as determined by the given components. A similar setting obtained on rotating the instrument 180° about its visual axis gives the brightness ratio for the remaining components.

light" through this combination, its apparent color, by virtue of the rotatory dispersion of the quartz, can be changed by rotating the analyzing Nicol and by varying the thickness of the quartz plate. With this simple combination, a limited range of colors

FIG. 13.



Polarization elements of the Arons chromoscope combined with a Lummer-Brodhun comparison cube.

results. Two such combinations in series—obtained by adding a second variable thickness rotatory plate and a variable azimuth Nicol between the polarizer and the light source—make up the complete instrument. With a definite "white light" source, any mixed color can be matched and therefore specified by the respective azimuths of the first and third Nicols relative to the second and the thickness of the two quartz plates.

Aside from its value in specifying and reproducing colors Priest has made an important application of the principle of rotatory dispersion to obtain from a practical light source whose color temperature was 2848° K., a luminosity distribution equivalent to that of a theoretical black-body at temperatures ranging from about 1800 to $24,000^{\circ}$ K.⁹

He has made another important application, namely, to produce a variable blue filter for eliminating color differences in heterochromatic photometry.¹⁰

4. *Pyrometry. Leucoscope Used as an Optical Pyrometer.*—In this,¹¹ the two contiguous images of a rectangular aperture formed by a Wollaston prism are viewed through an analyzing Nicol and a plate of right or left rotating quartz. In general with a heterochromatic source these differ in brightness and in color. A Nicol interposed between the source and the Wollaston may be adjusted in azimuth to produce a brightness match, and the analyzing Nicol may be adjusted in azimuth to approximate a color match. With a 20 mm. thickness of quartz, one part of the field will be a very pale blue and the other a very pale yellow, neither being recognized as more reddish than the other. This is the criterion for a setting. Other conditions remaining the same, the setting of the analyzing Nicol varies uniquely with the spectral distribution (color temperature) of the source. It may therefore be used as an optical pyrometer where the radiation by the source approximates sufficiently that of the ideal black-body. High precision is not possible, however, because of the necessity of judging quality of color, which is not so reliable as judging equality of brightness. Furthermore, each observer must use his own calibration. Where high precision is not so important as convenience, the leucoscope may prove to be a very useful pyrometer.

VII. ELLIPTIC POLARIMETERS.

1. *Elliptic Compensators.*—Here also, because of their admitted superiority, we shall confine our review to instruments whose criterion for a setting is a brightness match between con-

⁹ Priest, I. G., *Jour. Opt. Soc. Am.*, 5, p. 178 (1921); 7, p. 78 (1923); B. S. Sci. Paper No. 443 (1922).

¹⁰ Priest, I. G., *Phys. Rev.* [2], 9, p. 341 (1917); B. S. Sci. Paper No. 443 (1922).

¹¹ Priest, I. G., *J. O. S. A.*, 4, p. 448 (1920).

tiguous parts of the field of view—that is to half-shade instruments. All elliptic polarimeters are of the compensator type, in which the given elliptic vibration is “restored” to a rectilinear or definite elliptic vibration either by a variable order (thickness) doubly refracting plate or by a variable azimuth plate. From the azimuth and order of the compensator and the azimuth of the restored vibration, the constants of the given elliptic vibration are calculated. The variable thickness compensator is readily obtained, as illustrated in Fig. 14, by cutting a plane parallel doubly refracting plate into two wedge-shaped parts and pro-

FIG. 14.

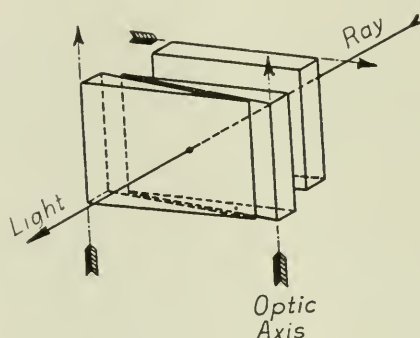


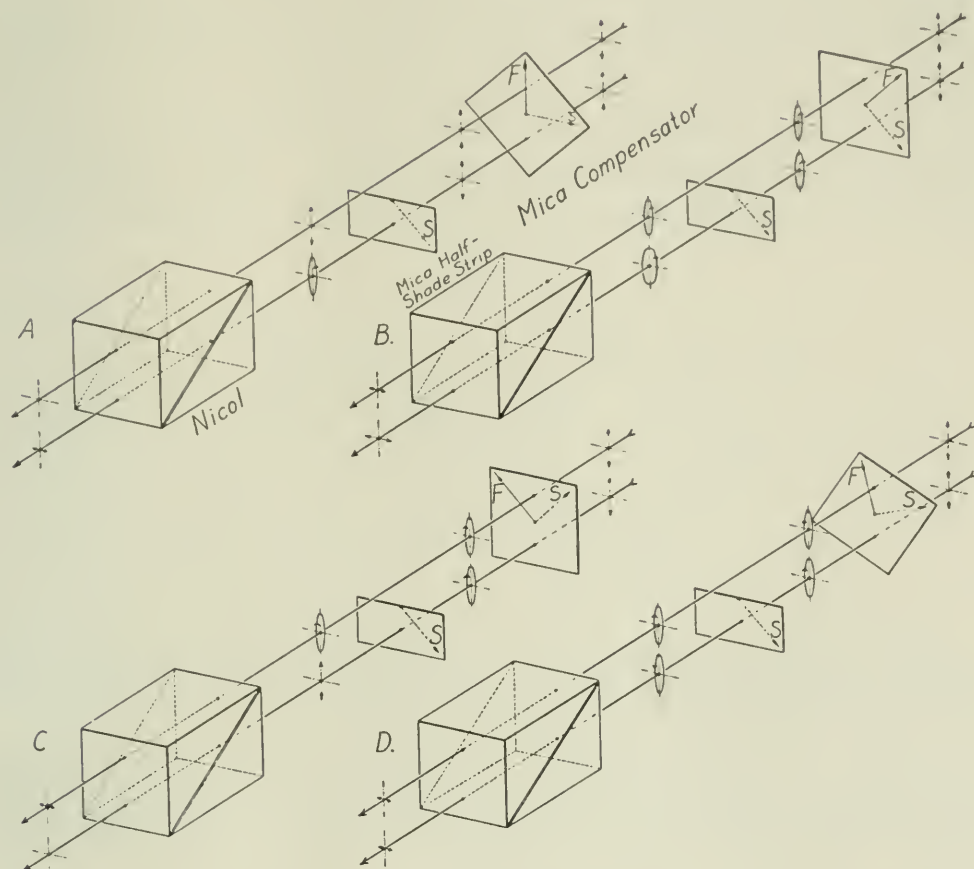
Diagram of Soleil-Babinet compensator for restoring elliptic to rectilinear vibrations.

viding for a measurable relative displacement in this plane. A continuous variation from positive to negative order is obtained through the addition of a second opposing plate, equal in its order to the wedge-pair at some intermediate thickness. This is the principle of the Soleil-Babinet compensator which, however, should not be confounded with the Babinet compensator—a device employing the shift of interference fringes instead of a brightness match.

The variable-azimuth compensator is very simple in design and construction. A uniform sheet of mica, having an order of a quarter-wave, mounted on a graduated circle, makes one which covers all ranges of ellipticity as noted in Section IV. Unfortunately, however, because of dispersion, a quarter-wave plate for one color is effectively less than a quarter-wave for all others—maximum ellipticity being introduced by odd multiples of a quarter-wave relative retardation (Fig. 7). It follows that the use of a variable-azimuth compensator is attended with the necessity of changing compensators when the color is changed,

if maximum range of compensation is desired. Even then, however, the increased uniformity of the field as compared with that of the wedge compensator makes the variable-azimuth type preferable.

FIG. 15.



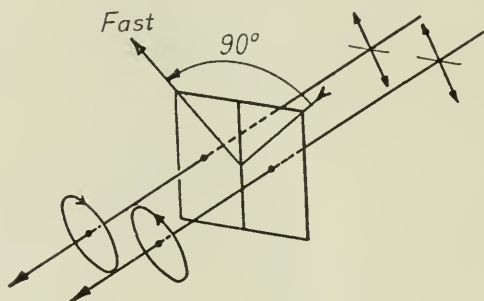
The Brace half-shade elliptic analyzer. Measures small ellipticities with high precision, but azimuths with low precision. (Order of half-shade strip, $.01$ to $.03\lambda$; compensator, $.02$ to $.06\lambda$ azimuth of half-shade near 45° .)

- A. Plane polarized entrant light; compensator in neutral position; half-shade strip produces positive ellipticity; viewed through Nicol, lower half of field bright, upper dark.
- B. Compensator produces positive ellipticity; half-shade strip augments it; lower half of field of view the brighter.
- C. Compensator produces negative ellipticity; half-shade strip restores it to a rectilinear vibration; upper half of field of view bright, lower dark—the reverse of "A".
- D. Compensator produces negative ellipticity supposedly equal to one-half that in "C"; half-shade strip converts it into an equal positive ellipticity; field of view matched—giving a setting.

2. *Elliptic Half-shades.*—The function of elliptic half-shades is the same as that of azimuth half-shades, namely, to show by an increased brightness of the one part simultaneous with a decreased brightness of the contiguous part, any deviation from the equality of brightness indicative of the correct setting of the compensator. Analogous to azimuth half-shades in which, assum-

ing equal transmission, the rectilinear (equal ellipticity) vibrations in the two parts respectively diverge by equal and opposite amounts from the matched azimuth of the analyzing Nicol, we have in the elliptic half-shade equal and oppositely traced ellipses of practically equal azimuth. The analyzing Nicol set "across" the common azimuth of these two ellipses gives a match. Any small change of the compensator from the correct setting decreases the magnitude of the ellipticity on the one part and at the same time increases it by an equal amount on the other, changing the relative brightness accordingly. Fig. 15 illustrates how this is brought about by a Brace elliptic half-shade¹² which

FIG. 16.



Bravais bi-plate. A "balanced" elliptic half-shade, the two parts being of equal and opposite order—approximately quarter-wave. The function of this half-shade is similar to that of the Brace, namely, to introduce equal and opposite ellipticity in the two parts of the field. Working azimuth should be small to avoid too high brightness levels.

is superior in its photometric fulfilments to all others, though less simple in theory than the so-called balanced half-shades such as the "Bravais bi-plate" illustrated in Fig. 16, which would be an ideal elliptic half-shade were it not impossible to obtain a vanishing dividing line between the parts of the field. With azimuth half-shades, the half-shade system is commonly a fixed part of the polarizing system, but not necessarily so, it might just as well be a fixed part of the analyzing system. On the other hand, while the elliptic half-shade can be a fixed part of either polarizer or analyzer, it is more commonly a part of the analyzer. The brightness level of the elliptic half-shade (which, like that of the azimuth half-shade, determines its sensibility) is readily varied from zero to a maximum by changing its azimuth, relative to the Nicol, from zero to 45° . The Brace half-shade is best when its order is so small as to require it to be used at the 45°

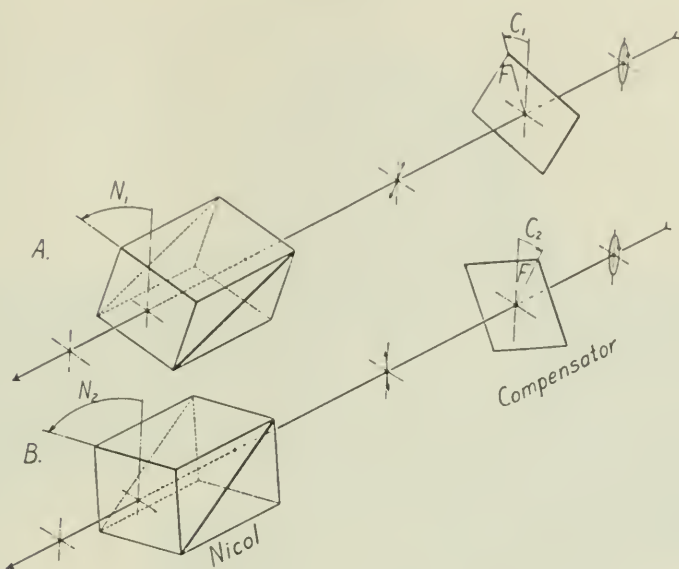
¹² Brace, D. B., *Phys. Rev.*, **18**, p. 70 (1904) ; **19**, p. 218 (1904).

azimuth, while the Bravais bi-plate must generally be used at a much smaller azimuth.

VIII. A GENERAL POLARIMETER.

For the combined determination of azimuth and ellipticity Tool's application of the Brace elliptic half-shade to the Stokes' method of analysis is the most accurate. In the Stokes' method¹³

FIG. 17.



The Stokes elliptic analyzer.

A. The compensator and Nicol are adjusted to give minimum intensity of field (restored polarization) and their respective azimuths C_1 and N_1 recorded.

B. The same is repeated with the compensator at a complementary azimuth—observed values C_2 and N_2 .

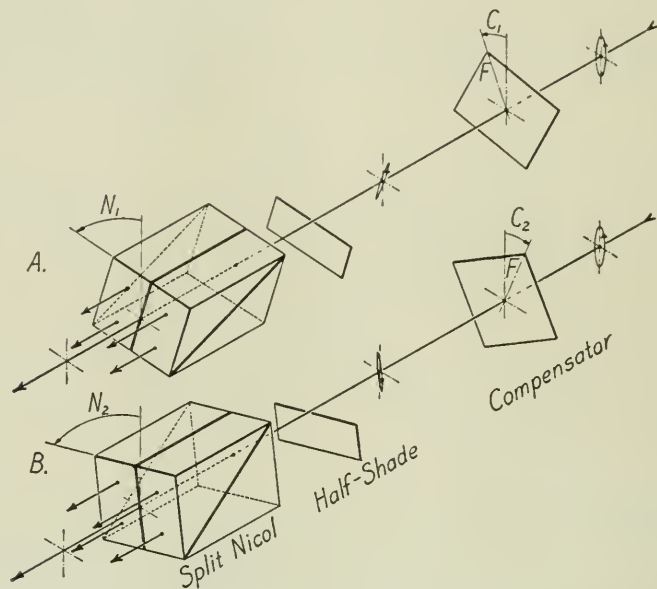
From the four azimuths C_1 , C_2 , N_1 and N_2 , both the ellipticity and the azimuth of vibration of the entrant light is determined. Will not measure a circular vibration.

(Fig. 17), the given elliptic vibration whose azimuth and ellipticity are sought, is restored to a rectilinear vibration by passage through a mica plate, for example, first in one azimuth, then in its complementary azimuth. The analyzing Nicol is set for extinction on the two restored vibrations, the corresponding azimuths of the compensator being observed. From the complementary azimuths of both Nicol and compensator, the azimuth and ellipticity of the given elliptic vibration is calculated in a relatively simple manner, in which process the order of the compensator does not need to be known. While this method is extremely simple, it is not so accurate as generally desired. By substituting a Cornu-Jellett half-shade Nicol for the simple analyzing Nicol

¹³ Stokes, C. G., *Phil. Mag.* [4], 2, p. 420 (1851).

of Stokes and fixing to this a Brace elliptic half-shade so as to give a four-part field, Tool¹⁴ makes complementary settings for a four-part match of the field, and carries out computations analogous to those of Stokes to obtain the constants of the given elliptic vibration. This instrument is diagrammatically illustrated in Fig. 18. With a balanced elliptic half-shade, the formula used would be the same as that for the Stokes instrument;

FIG. 18.



Tool's azimuth and elliptic half-shade combination. Replaces the Nicol in Stokes' method with a Cornu-Jellett half-shade Nicol to which is attached a Brace elliptic half-shade. Complementary settings (*A* and *B*) for a match of the four-part field are made and computations analogous to Stokes' carried out. The compensator restores the given ellipticity, not completely, but to a definite small magnitude and the half-shade Nicol locates its azimuth.

but with a Brace half-shade, it is more complicated, requiring the order of the half-shade to be either negligible or known. Tool's measurements indicate for this instrument an accuracy better than 1 per cent. when measuring ellipticities of the magnitude of .02; and an accuracy of .05 per cent. in measuring circular vibrations—where the Stokes instrument fails.

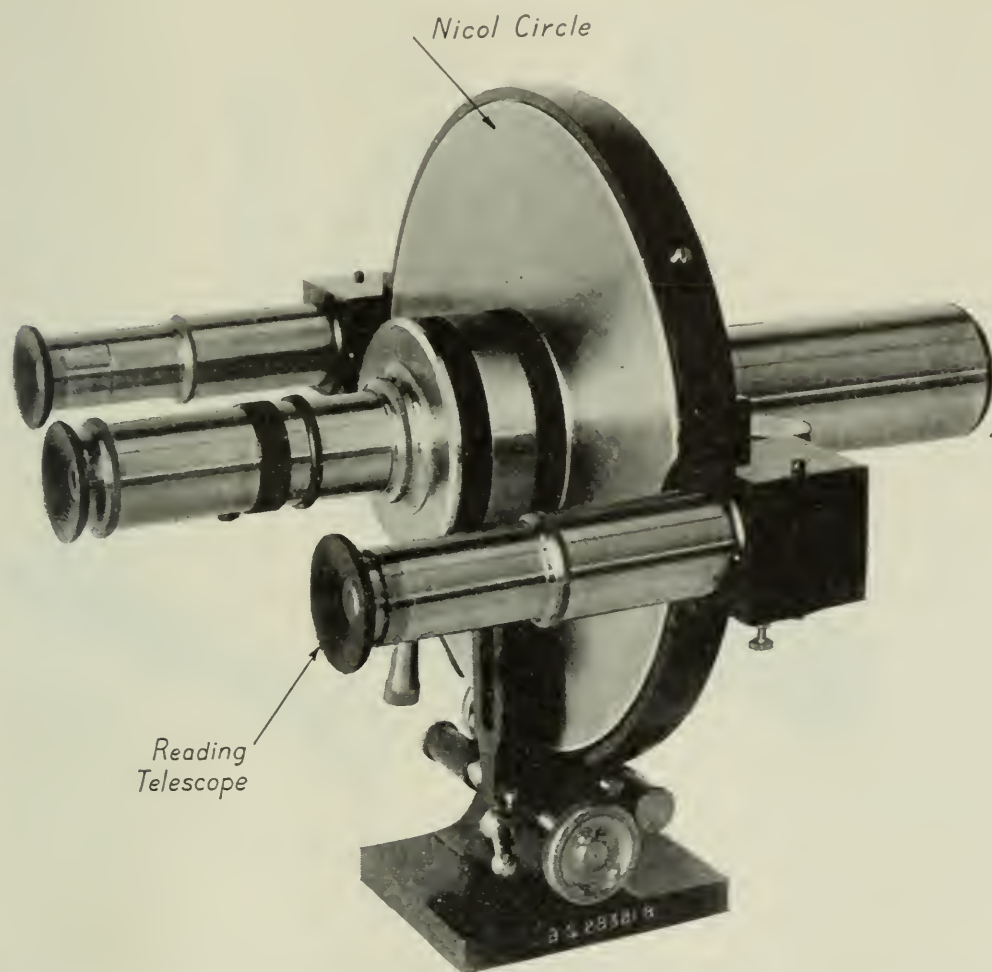
IX. A UNIVERSAL POLARIMETER.

There has been recently designed and constructed at the Bureau of Standards a polarimeter (Figs. 19*a* and *b*) which is readily convertible into a convenient form for making any of the special measurements reviewed above. For purely azimuth measurements

¹⁴ Tool, A. Q., *Phys. Rev.*, 31, p. 1 (1910).

of plane polarized light, Tool's general polarimeter would obviously be too cumbersome. Furthermore, for measuring small ellipticities without reference to their azimuth, the Brace type is much more convenient than that of Tool. A detailed description and working theory of this *universal polarimeter* is to be pub-

FIG. 19a

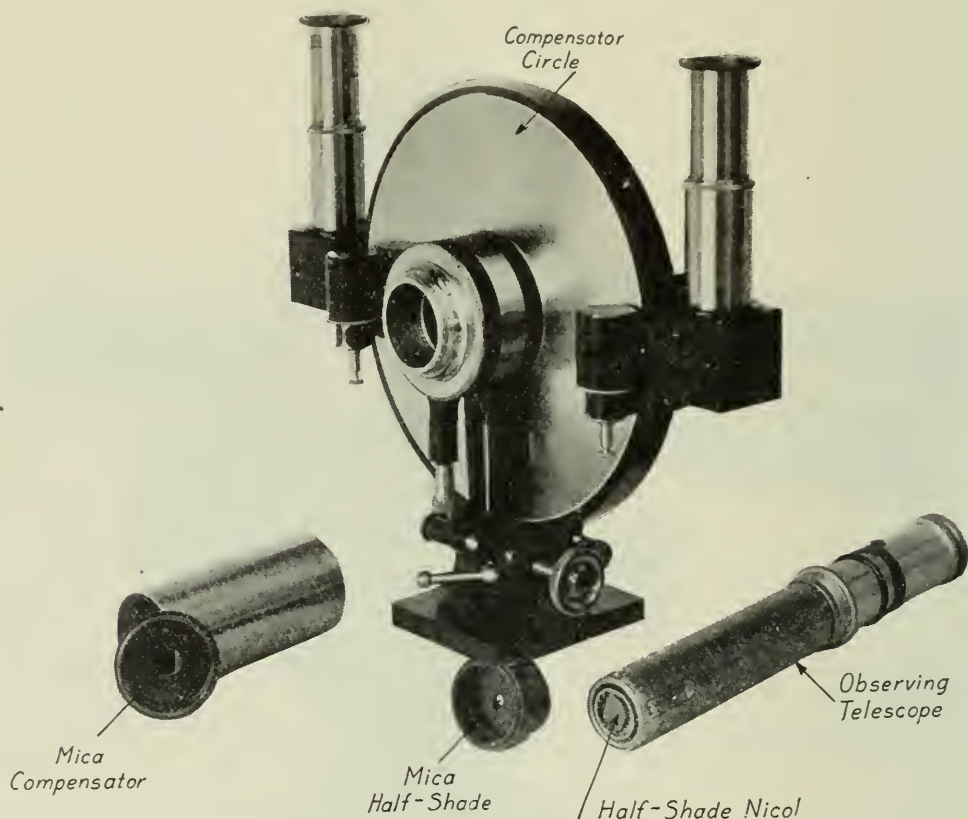


Assembled view of universal polarimeter designed to be mounted on the telescope arm of a spectrometer.

lished shortly so that a brief enumeration of its features will suffice here. As shown in the figures, it is assembled as a Tool polarimeter. The light to be measured is passed, as in Fig. 18, first through a mica compensator carried by the "compensator circle" (which is graduated on its edge), then through the mica elliptic half-shade and half-shade Cornu-Jellett Nicol mounted together on the extended end of the observing telescope

which is carried by a similar "Nicol circle." These two circles are respectively supported on the two ends of a central hub provided with a single pair of Vernier arms, each arm having two Verniers, one for each circle, reading to $.01^\circ$. Both circle scales are in the field of view of the reading telescope at the same time,

FIG. 19b.



Disassembled view of same reversed.

and the two reading telescopes can be used either in the position of 19a, by the observer, or in the position of 19b by an assistant. Slow motion of both circles is provided by the tangent screws at the base. To convert the instrument into a Brace elliptic polarimeter, the half-shade Nicol is replaced by a simple Nicol and a thin compensator used. To convert it into an azimuth polarimeter for rectilinear vibrations, the elliptic half-shade and compensator are both removed and a half-shade Nicol placed in either the analyzing or polarizing end of the system.

X. APPLICATIONS OF THE GENERAL POLARIMETER.

1. *Determination of the Optical Constants of Absorbing Media.*—One of the most important applications of the general polarimeter is in determining the refractive indices, absorption constants and reflecting power of metals and other highly absorbing materials capable of being given a mirror polish. This development, which the electromagnetic theory of light brought with it, was perhaps Drude's major contribution to physics.

By measuring the change in form of vibration which light suffers on reflection from a mirror, not only can the reflecting power be determined with an accuracy which other methods cannot attain, but also the refractive indices and absorption coefficients of the material can be deduced therefrom with a degree of precision which no other method can approach.

The method may be sketched as follows: Plane polarized light with its azimuth at 45° to the plane of incidence falls on the mirror at a definite angle. The azimuth and ellipticity of the reflected light is measured, and these magnitudes, together with the angle of incidence, serve to calculate the desired constants.

The change in azimuth arises from the component vibration parallel to the plane of incidence having a reflection coefficient different from the component perpendicular to it. Transparent media show a similar effect as illustrated by the "polarizing angle" at which the parallel component has a zero reflection coefficient. The change in ellipticity arises from a difference in the phase loss (or gain) of the two components on reflection. An application of the corresponding effect in transparent media is Fresnel's rhomb in which by two internal reflections at an angle of incidence of about 51° in glass, the parallel component leads the perpendicular component in phase by a quarter-wave—the rhomb thus serving as a quarter-wave plate.

The theory of the method for absorbing media is not simple, owing to the refractive index—and consequently also the *extinction* coefficient—varying with the angle of incidence. That such a variation is possible is readily appreciated from the fact that Fresnel's theory requires the direction of the ray in a transparent isotropic medium to be slanting to the wave-front instead of normal to it, if the amplitude of vibration varies along the wave-front. In an absorbing medium such a condition results from

different parts of the same wave-front having traversed different depths of the medium for other than normal incidence.

The reliability of the polarimetric method for determining the reflecting power of mirrors has been tested by Tate¹⁵ for normal incidence and by Wilsey¹⁶ for both components at slanting incidence.

2. *Mechanical Stress Analysis*.—The phenomenon called forth by mechanical stress is known as “accidental double refraction.” It was discovered by Brewster in 1816 and the first application made by Maxwell to study stress in the plane of a strained plate. In general, an isotropic solid such as glass becomes doubly refracting when subjected to stress. By compressing it in a direction at right angles to a ray passing through it, both the component vibration perpendicular to the direction of the compression and that parallel to it are usually slowed up in their velocity of propagation, the former more than the latter. On substituting a tension for the compression, the effect is exactly reversed, both components are accelerated in velocity, that at right angles to the tension, the most.

The result in general is that rectilinearly polarized entrant light is propagated through strained glass as two rectilinearly vibrating wave-trains, one with its azimuth in the direction of the stress and the other at right angles to it. The higher velocity train gains on the other by an amount proportional both to the thickness of the plate and to the magnitude of the stress. The emergent light becomes thus elliptically polarized, its form and azimuth serving to measure the magnitude and direction of the simple stress. In practical applications, the problem seldom has to do with a simple stress.

The purely mechanical methods by which an experimental solution of stress problems is attacked are both difficult and often questionable in their results. One has to assume at the start that the stress is proportional to the magnitude of the strain. This principle can hold only within the elastic limit of the material. Beyond the elastic limit, these methods fail entirely. Furthermore, stresses within the body cannot be measured by mechanical devices. The optical method has proved to be, there-

¹⁵ Tate, J. T., *Phys. Rev.* [1], 34, p. 321 (1912).

¹⁶ Wilsey, R. B., *Phys. Rev.* [2], 8, p. 391 (1916).

fore, very acceptable, though it is unable to furnish alone a solution of the problem. Happily, any combination of stresses in a plane at any point may be represented by an ellipse in that plane whose axes give the direction and magnitude of the so-called principal stresses. A ray of light passing through the strained medium perpendicular to the plane of this ellipse is propagated as two rectilinearly vibrating wave-trains whose vibrations are respectively parallel to these two principal stresses. The difference in velocity of propagation of these two trains has been found to be simply proportional to the *difference of the principal stresses*, so that the optical method furnishes a measure of *this difference only*, not of the stresses themselves. If the circumstances dealt with are of a nature such that Poisson's ratio can be applied to determine the *sum of the stresses*, then the two determinations together serve to solve the problem.

During the last few years, this subject has been attacked with vigor and with a very satisfactory measure of success by a number of investigators, among whom are Professors Filon and Coker and Major Low of England, and M. Mesnager of France.

A discovery which has proved to be specially contributory to this success was made by Coker, that xylonite (celluloid) is a very satisfactory material to use for the purpose. It lends itself especially well to both the optical and mechanical determinations, in that it possesses large accidental double refraction and can readily be worked into form. An appreciable "skin effect" is perhaps its worst feature.

Perhaps the most notable application of optical stress analysis has been made by Mesnager who, from a glass model, made a determination of the stress distribution in a bridge of reinforced concrete to be placed over the Rhone at Balme.

3. *Optical Homogeneity of Glass.*—Optical glass, especially molded pieces, is found to be bi-refringent if it has not been properly annealed. If very bad, the piece will crack in cooling or under the process of grinding. If not so bad, the refracting or reflecting surfaces may simply be distorted in the grinding and polishing, thereby giving poor images. If neither of these troubles arises, there still remains the possibility of a "fuzzy" image—though it may be open to question whether the fuzziness observed is due to strain or arises from other inhomogeneities. In any case, whatever the immediate effect, it remains that the

presence of imperfect annealing is readily revealed in both quality and degree by polarimetric measurements, and such measurements are used for determining the acceptability of glass for optical purposes.

XI. SUMMARY.

A review of those fundamental facts and relations concerning polarized light with which the reader should be familiar is given. The devices which serve as the polarization elements of all instruments are then described, followed by a description of half-shade azimuth polarimeters, elliptic polarimeters, Tool's general polarimeter, and a Universal polarimeter designed at the Bureau of Standards.

The practical applications of polarimeters to saccharimetry, photometry, colorimetry, pyrometry, determination of the optical constants of absorbing media, mechanical stress analysis and testing of the optical homogeneity of glass are all briefly described.

The Mechanism of "Dry Corrosion."—Under this term is to be understood the corrosion of metals exposed to air, but protected from rain. The subject has been investigated by U. R. Evans, whose paper has been published by the Faraday Society, as part of a symposium on corrosion of industrial metals. The metals examined were roughened with emery. No corrosion occurred when kept over sulphuric acid, and very little when kept over water. The rate of attack is much increased if volatile electrolytes are in the air, sulphur dioxide being especially dangerous to iron and nickel, ammonia to copper, hydrogen chloride to zinc and aluminum. Hydrogen sulphide and carbon dioxide increase somewhat the rate of rusting of iron, but only superficial changes on other metals.

Evans thinks that the change is due mainly to the influence of the film of moisture on the surface of the metal. This is, of course, invisible, but generally present. Volatile electrolytes increase the conductivity of the film because they are absorbed by it, and as in many cases they may tend to form hygroscopic compounds, the thickness of the film will be increased. In some cases (zinc in hydrogen chloride, copper in ammonia, nickel in sulphur dioxide) the metal originally dry soon begins to shed moisture, and in such cases, corrosion is serious.

The paper was subjected to discussion by several persons, and some exception was taken to the author's statements and conclusions.

H. L.

THE PRESSURE EFFECT AND OTHER PHENOMENA IN GASEOUS DISCHARGES.*

BY

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WHEN an electric discharge of rather high current density is passed through a monatomic gas at low pressure, the gas tends to move towards the anode and causes the pressure at the anode to exceed that at the cathode. This pressure effect has been observed and studied by L. Hamburger,¹ F. Skaupy² and A. Rüttenauer.³ Hamburger and Skaupy have attempted to explain the motion of the gas to the anode by assuming the presence of negative ions having a mobility higher than that of the positive ions. Skaupy,⁴ in a later paper, considers that the effect may be due to the fact that electrons make elastic collisions with atoms while positive ions make inelastic collisions. Thus he assumes that the electrons deliver twice their momentum to gas molecules (because they rebound), while the positive ions cannot deliver more momentum than corresponds to their velocity. A little analysis shows, however, that there is a fallacy in this argument since the rebounding electrons would subsequently collide with other atoms and thus deliver momentum in the opposite direction. In fact, it is readily seen that the effect is thus neutralized. Since positively and negatively charged particles must be present in equal numbers in any uniformly ionized gas, the momenta delivered by the electric force to the positive and to the negative particles in each unit of time must be equal and opposite. Thus, *as long as the particles remain in the gas*, there is no resultant force acting on the gas.

Hamburger's and Skaupy's experiments have been cited by Franck and Grotrian⁵ as evidence for the existence of negative ions in discharges in such gases as argon, which have been thought to have no appreciable electron affinity.

Let n_e , n_p and n_n be respectively the number of electrons, positive ions and negative ions per unit volume and let v_e , v_p and v_n be the corresponding average velocities parallel to the axis

* Communicated by the Author.

of the discharge tube. Then, since there can be no appreciable space charge in any uniform positive column,

$$n_e + n_n = n_p, \quad (1)$$

assuming that both the positive and negative ions are univalent. If i is the current carried by the discharge then (taking all velocities positive)

$$i/e = n_e v_e + n_n v_n + n_p v_p. \quad (2)$$

The number of molecules of gas which drift towards the anode through any given cross-section is $n_n v_n - n_p v_p$. Thus if $n_n v_n$ is greater than $n_p v_p$, the gas will be carried electrically towards the anode. As the pressure at the anode increases, gas flows back through the tube to the cathode, but the viscosity of the gas makes it necessary for the pressure at the anode to rise to a certain limiting value before a steady state is reached. Experiments have usually shown⁶ that the mobility of negative ions is somewhat larger than that of positive ions, but the difference is not large, the ratio of the mobilities ranging from 1.0 to 1.6. Thus to cause an increase in pressure at the anode, n_n would have to be at least 60 per cent. of n_p . It is well known that electrons attach themselves to molecules in electronegative gases such as oxygen at high pressures, but the data of Townsend,⁷ Loeb⁸ and others seem to indicate that there is no such tendency in the inert gases. However, in these experiments negative ions would have been detected only if the current carried by the negative ions had been appreciable in comparison with that carried by electrons. The mobility of the electrons in argon may be assumed to be of the order of magnitude of $\sqrt{1834 \times 40}$, or 271 times that of the ions. Thus we may assume as an example within the range of possibility: $v_e = 271 v_p$; $v_n = 1.6 v_p$; $n_n = 0.7 n_p$ and thus find by Equation (1) that $n_e = 0.43 n_n$ and by Equation (2) that the current carried by negative ions ($n_n e v_n$) is only 0.014 of that carried by electrons ($n_e e v_e$), even under these conditions which would cause gas to accumulate at the anode. Although it appears *probable* from the work of Townsend and others that the current carried by negative ions in argon is much less than 1 per cent. and therefore cannot explain the pressure effect in this gas, yet it cannot be said that the experiments have proved this point.

In connection with a study of the positive column of the mercury arc, the writer has, however, developed a theory capable

of explaining the increase of pressure at the anode without the necessity of assuming negative ions. By measuring the volt-ampere characteristics of small electrodes in the path of the discharge, at low pressures, such as ten bars, it has been found that the electrons in a given volume move nearly in random directions with an average kinetic energy which is independent of the current density in the arc (in the range from 0.1 to 1.0 ampere per square centimetre) but which depends on the mercury vapor pressure as shown in Table I.

TABLE I.
Kinetic Energy of Electrons in the Mercury Arc.

Temp. of Mercury.	Pressure of Vapor. Bars	Average Kinetic Energy. Volts	Equivalent Temp.
15°C.	1.0	3.9	30000°K.
32°C.	4.4	2.9	22400°K.
60°C.	33.	1.7	13900°K.

The third column gives the potential difference through which electrons must fall to acquire a kinetic energy equal to the average kinetic energy of those in the arc. The distribution of velocities about the mean has been found to correspond to that given by Maxwell's law. The kinetic energies of the electrons are thus the same as those of molecules in gases at the temperatures given in the fourth column.

A negatively charged electrode in the ionized gas of the arc repels electrons from its neighborhood, so that there is a positive ion sheath around the electrode.⁹ By calculation from the space charge equations, it is found that the thickness of this sheath is usually not more than about 0.1 mm. The sheath acts as an electrostatic screen so that the field due to the negative charge on the electrode does not extend beyond the edge of the sheath. All positive ions that reach the sheath are attracted to the electrode. If the electrode is large compared to the sheath thickness, the positive ion current that flows to the electrode is thus practically independent of the applied voltage, and is a true measure of the *positive ion current density* I_p in the arc.

When the electrode is positively charged and the gas pressure is not too high, an electron sheath is formed in a similar manner and the electron current over a certain range is nearly independent

of the applied voltage and is a measure of the *electron current density* I_e in the surrounding space.

The ratio $I_e : I_p$ is nearly the same at different current densities or mercury vapor pressures and averages about 340:1. The value of I_e may be too low because of the reflection of some electrons, whereas ions are apparently not reflected to an appreciable degree.

If the kinetic energy of the electron is the same as that of the ions, the ratio should be equal to $\sqrt{200 \times 1834} = 605$. The experiments prove conclusively, however, that the current carried by electrons in the mercury arc is *at least* 340 times that carried by positive ions.

The glass wall of the tube (or any isolated electrode) must acquire such a potential that it receives the same number of negative and of positive charges. Thus it must be sufficiently negatively charged to repel at least all but one electron out of every 340 that move towards it. To do this the walls need to have a negative potential with respect to the surrounding space, which, according to the Maxwell law, is roughly four times the potential corresponding to the average energy of the electrons; according to Table I the walls will thus be from 7 to 16 volts negative, depending on the mercury vapor pressure. It is clear that very serious errors are made by attempting to measure potentials in ionized gases by using sounding electrodes.*

There[†] are, however, two simple methods by which the true space potentials can be measured. In the first method a tungsten filament is used as sounding electrode, so arranged that it can be heated when desired. The filament is first heated to a temperature just below that at which there is appreciable electron emission, but a key is arranged to short-circuit a part of the resistance in series with the filament and thus momentarily raise its temperature to a point where it is capable of emitting an easily measurable current. The potential of this hot sounding electrode is then varied and at each potential it is noted whether or not the current

* Because of this error arising from the use of sounding electrodes, measurements of the anode drop have been altogether too high. In the mercury arc the anode drop is usually about 2 to 3 volts, whereas measurements with ordinary sounding electrodes show 10 to 18 volts. In some cases the anode drop is actually a few volts negative. The conditions at the anode and cathode will be discussed in subsequent articles.

to it changes when the temperature is altered by pressing the key. It is evident that the electrons emitted from the filament can escape only when there is an accelerating field around it. The filament is at the same potential as the space when the electrons are just able to escape. Small corrections need to be made for the voltage drop along the filament and for the initial velocities of the electrons emitted.

The second method consists in measuring the volt-ampere characteristics of a cold sounding electrode, preferably of such large size that its dimensions are fairly large in comparison with the thickness of the electron sheath that forms about it when it is positively charged. As the potential of the electrode is raised, starting from negative values, it first takes up positive ions, then also takes up high velocity electrons. At some definite potential it takes up all the electrons moving toward it (except those reflected); a further increase in potential causes no increase in electron current except as a result of an increase in the sheath thickness. By plotting the current on semi-logarithmic paper against the potential, it is thus found that there is a definite kink in the curve at the point when the electrode potential is the same as that of the surrounding space. This method is found to give results in good accord with those obtained by the hot sounding electrodes and both methods prove that the wall of the tube, or any electrode to which no current flows, is negatively charged with respect to the surrounding space by an amount usually ranging from 5 to 15 volts.

All but a minute fraction of the electrons moving toward the wall are thus *elastically reflected* in the positive ion sheath near the glass surface and are unable to deliver energy to the wall. Direct experimental measurements of the number of electrons striking the wall and comparison with the power consumed by the arc prove that 99.7 per cent. of the electrons moving towards the wall are reflected, and that these electrons lose less than 0.5 per cent. of their energy by such reflection. At first sight it would seem that the reflection should be specular, that is, that there should be no change in average momentum parallel to the axis of the tube. Experiments which will be described in a subsequent paper seem to prove, however, that the reflection is about 30 per cent. diffuse, the collisions of an electron with the wall having the effect of reducing the average longitudinal velocity component

by about one-third. This effect is made manifest particularly by the action of transverse and longitudinal magnetic fields, which change the number of collisions of electrons with the walls, without altering the number of collisions with gas atoms. It is perhaps possible that the diffuseness of the reflection is due to the fluctuations of the positive ion space density in the sheath resulting from statistical causes.

Both theory and experiment, however, indicate that the positive ions are absorbed by the wall and deliver to it all their energy and momentum.

HEATING OF THE WALL BY POSITIVE IONS.

Let us assume that the electrons and the positive ions have an average kinetic energy corresponding to a voltage V_o . Let I_p be the current density of positive ions striking the wall (amperes per cm.²). There will be an equal number of electrons striking the wall to neutralize the charges of the ions. The energy corresponding to the ionizing potential (10.4 volts) will be liberated presumably in the form of heat when the positive ion and the electron combine. Let V_s be the potential drop through the sheath, near the glass surface. The energy carried to the wall by the positive ion in the form of kinetic energy thus corresponds to $V_s + (4/3)V_o$. The factor $4/3$ comes from the fact that the kinetic energy of particles passing a given plane ($2kT$) is $4/3$ times as great as that of the particles in a given volume ($3/2$) kT . The energy of the electrons striking the walls is $(4/3) V_o$. The total energy corresponds to $10.4 + V_s + (8/3) V_o$ volts.

In an experiment with a four-ampere arc flowing through a tube 3.2 cm. in diameter with mercury vapor at a pressure of 1.0 bar, the positive ion current density I_p was found to be 0.0011 ampere per cm.² Taking $V_o = 3.9$ volts, from Table I, and $V_s = 16$ volts, we should get a heating effect corresponding to 37 volts. Thus 37×0.0011 , or 0.042 watt, should be liberated as heat on each square centimetre of tube surface as a result of the positive ion bombardment. As the voltage drop in the arc was 0.24 volt per centimetre, the total energy per second generated in the arc per square centimetre of wall was 0.095 watt. Thus 44 per cent. of the power consumed in the arc path was liberated on the walls as a result of the positive ions striking the walls.

At higher mercury vapor pressure the percentage of heat thus carried to the wall decreased and it also decreased as the arc current decreased. Thus in a six-ampere arc with a pressure of 15 bars, 23 per cent. of the energy consumption was caused by positive ions, but at the same pressure with an arc current of one ampere, the percentage was only 15.

PRESSURE EFFECT DUE TO POSITIVE ION IMPACTS ON WALLS.

The positive ions that strike the wall of the tube have an average velocity component v_x in the direction towards the cathode. Let m_p be the mass and e the charge of a positive ion. The force p_x exerted by the ion impacts on each unit area of the inner surface of the tube in a direction towards the cathode is thus

$$p_x = \frac{\varepsilon m_p v_x I_p}{e} \quad (3)$$

since the number of ions striking unit area per unit time is I_p/e . The factor ε is a number less than unity which represents the degree to which the reflection of the electrons by the wall may be regarded as being specular. This factor seems to be approximately of the order of 0.3.

The reaction from this force p_x must be exerted in the gas and must tend to cause an increase in pressure at the anode. It is easy to understand the mechanism of this reactive force. We have seen that the forces due to impacts of ions and electrons against atoms must balance one another in any mass of ionized gas containing equal numbers of positive and negative charges, as long as all the accelerated particles remain within the gas. But when positive ions leave the gas the impact of the electrons against the atoms, producing a force acting towards the cathode, is no longer balanced by the impacts of the positive ions against the atoms.

If the gas pressure is so low that the normal mean free path λ_n is large compared to the radius r of the tube, the gas moves towards the anode until the increase in pressure there balances the force due to p_x , but at higher gas pressure the force p_x causes the gas near the wall to move towards the anode while the gas near the axis of the tube will move in the opposite direction, the increase in pressure at the anode being thereby decreased.

At higher pressures the reactive force due to the positive ion impacts on the wall may thus be assumed to be exerted on the

gas at a distance $r - \lambda$ from the axis of the tube; the gas at this point will have the greatest velocity towards the anode. Let v be this velocity. Then between r and $r - \lambda$ the volume of gas flowing per unit time will be $\frac{1}{2}v\pi[r^2 - (r - \lambda)^2]$. If no gas should flow back along the axis of the tube (because of the increased pressure near the anode), the volume of gas flowing per unit time between 0 and $r - \lambda$ would be $v\pi(r - \lambda)^2$. But by Poiseuille's law, the volume of gas per unit time that flows back because of the pressure gradient is $\frac{\pi}{8} \frac{(r - \lambda)^4}{\eta} \frac{dp}{dx}$, where η is the coefficient of viscosity. In a steady condition with a discharge tube closed at the end, the total amount of gas flowing through the tube must be zero, so that we have

$$v = \frac{r^2}{8\eta} \left(1 - \frac{\lambda}{r}\right)^3 \frac{dp}{dx} \quad (4)$$

if we neglect $\frac{1}{2}\lambda^2$ in comparison with r^2 .

Besides the force p_x (per unit area) acting on the wall of the tube due to the impact of positive ions, there is also a force p_a due to the impact of neutral atoms because the gas at $r - \lambda$ is moving towards the anode with the velocity v . The number of atoms per unit area per unit time striking the wall of the tube is $p(2\pi MRT)^{-\frac{1}{2}}$ and of this the fraction $(r - \lambda)/r$ may be assumed to have come from the region where the velocity is v . Thus we find

$$p_a = pv \left(1 - \frac{\lambda}{r}\right) \sqrt{\frac{M}{2\pi RT}}. \quad (5)$$

Here M is the atomic weight of the gas and R is the gas constant per gram molecule 8.37×10^7 ergs per degree.

The actual force per unit area acting on the wall of the tube is thus $p_x - p_a$ and this multiplied by the circumference of the inside of the tube must be equal to the pressure gradient multiplied by the cross-section, so that

$$r \frac{dp}{dx} = 2(p_x - p_a) \quad (6)$$

Eliminating v and p_a from Equations (4), (5) and (6) and solving for $\frac{dp}{dx}$, we find

$$\frac{dp}{dx} = \frac{2p_x/r}{1 + \frac{rp}{4\eta} \left(1 - \frac{\lambda}{r}\right)^4 \sqrt{\frac{M}{2\pi RT}}} \quad (7)$$

This equation is derived for the case that the pressure is so high that λ_n is smaller than $\frac{1}{2}r$. At lower pressure where $\lambda_n > r$, the equation reduces to

$$\frac{dp}{dx} = \frac{2p_x}{r} \quad (8)$$

To calculate p_x we need to know the velocity component v_x of the ions in the direction of the field.

The time taken by an ion to travel a free path λ with the velocity Ω is λ/Ω . If γ is the acceleration due to the field, then the velocity component in the direction of the field, acquired during the average path, is given by

$$\frac{dx}{dt} = \frac{\gamma\lambda}{\Omega} \quad (9)$$

This equation has been derived by G. Hertz¹⁰ for the velocity of drift of electrons in a field. Because of the persistence of velocities of the ions after collisions¹¹ this should be multiplied by 1.26. Since the acceleration is $(e/m_p)(dV/dx)$, we have

$$v_x = 1.26 \frac{e\lambda}{m_p\Omega} \frac{dV}{dx} \quad (10)$$

The average velocity Ω of the ions in a given volume may be calculated from V_o , the potential corresponding to the average kinetic energy of the ions in a given volume by the relation

$$\Omega = \sqrt{\frac{16 V_o e}{3\pi m_p}} \quad (11)$$

Combining Equations (10) and (11)

$$v_x = 0.96 \sqrt{\frac{e}{m_p V_o}} \frac{dV}{dx} \quad (12)$$

and by Equation (3)

$$p_x = 0.96 \epsilon \lambda I_p \sqrt{\frac{m_p}{e V_o}} \frac{dV}{dx} \quad (13)$$

If we express p in dyne cm.⁻², x and λ in cm., I_p in amps. cm.⁻², V in volts, and insert the values $e = 1.591 \times 10^{-20}$ e. m. units and $m_p = M \div 6.06 \times 10^{23}$, the equation becomes

$$p_x = 9.80 \epsilon \lambda I_p \sqrt{\frac{M}{V_o}} \frac{dV}{dx} \quad (14)$$

In this equation, as well as those immediately preceding, λ is not the normal free path which would occur in a large volume, but is the average actual free path which at low pressures is limited by

the wall of the tube. Where λ_n is larger than r , the value of λ should then be put equal to $2r$, the diameter of the tube.

The pressure effect may now be calculated by combining Equations (14) and (8)

$$\frac{dp}{dx} = 18.6 \epsilon I_p \frac{\lambda}{r(1 + \rho)} \sqrt{\frac{M}{V_0}} \frac{dV}{dx} \quad (15)$$

where for convenience the second term in the denominator of the second number of Equation (7) has been represented by ρ . Putting in the numerical value of R , we thus have

$$\rho = 1.09 \times 10^{-5} \frac{r p}{\eta} \left(1 - \frac{\lambda}{r}\right)^4 \sqrt{\frac{M}{T}}. \quad (16)$$

Rüttenauer measured the pressure effect in helium and argon at pressures ranging from 700 to 1200 bars, current densities from 0.6 to 1.6 amperes per cm.² with an arc in a tube 0.75 centimetre in diameter. Within the relatively narrow ranges covered by these experiments, he was able to express his results for the pressure gradient by the empirical equation

$$\frac{dp}{dx} = C \frac{I \sqrt{M}}{p} \frac{dV}{dx} \quad (17)$$

where C is a constant, and I is the current density in the arc. Expressing p in bars, I in amps. cm.⁻², V in volts, x in cm., the value of the constant best fitting the results is $C = 77$.

Comparing Equations (15) and (17) we see that they are in many respects similar. If the two equations are to give the same value for $\frac{dp}{dx}$, we must have

$$\frac{I \sqrt{V_0}}{I_p} = 0.241 \frac{\epsilon \lambda p}{r(1 + \rho)} \quad (18)$$

The temperature of the gas in the tube may be assumed to be roughly 1000° K. The viscosities¹² of helium and argon at this temperature are given in Table II. The free path at the average pressure (900 bars) is calculated from the viscosity in the usual way. The quantity ρ is found from Equation (16). The values of

TABLE II.

Analysis of Rüttenauer's Data on the Pressure Effect.

Gas.	η	λp	λ/r	ρ	$\frac{I \sqrt{V_0}}{\epsilon I_p}$	$\sqrt{\frac{m_p}{m}}$
He	4.25×10^{-4}	115	0.34	0.10	67	86
A	5.6×10^{-4}	48	0.14	0.71	18	273

$I\sqrt{V_o}/(\epsilon I_p)$ which have been calculated by Equation (18) are reasonable. The experiments with the mercury vapor arc give the ratio $I_e : I_p = 340 : 1$, but the true value may lie close to $605 : 1$, which is the square root of the ratio of the mass of the mercury ion to that of the electron. Because of elastic collisions between the electrons and the mercury atoms and the walls of the tube, the electron current density I_e is sometimes as much as twenty times as great as the apparent current density I in the arc. Therefore, in general, we may assume that I/I_p may be several times less than $\sqrt{m_p/m}$. The data of Table II show that the ratio of $\sqrt{m_p/m}$ to $I/\epsilon I_p$ is equal to about 1.3 for helium and 1.5 for argon.

Rüttenauer finds that when the pressure is lowered, $\frac{dp}{dx}$ reaches a maximum and slowly decreases. An arc in argon with a current of 0.16 ampere in a tube 0.75 centimetre diameter gave a maximum pressure gradient of 1.86 bars per centimetre at $p = 600$ bars; 1.63 at 333; 1.30 at 133, and 0.97 at 75 bars. As the potential gradients were not recorded these data cannot be used directly to test the equations. It is clear, however, from Equation (15) that as the pressure decreases the gradient should increase about inversely proportional to the pressure until λ becomes about equal to the diameter of the tube. At lower pressures λ must be considered to remain approximately constant. The decrease in the gradient at still lower pressure is probably accounted for by the increase in V_o as was found for the case of mercury (Table I).

SUMMARY.

In the positive column of the mercury arc the electrons have velocities distributed in accord with Maxwell's law, and the directions of motion are distributed nearly at random. The average velocity of the electrons is approximately independent of the arc current but depends on the pressure. The average kinetic energy of the electrons, expressed in terms of the corresponding voltage, is 3.9 volts at 1 bar pressure, 2.9 at 4.4 bars and 1.7 at 33 bars.

Isolated electrodes, or glass surfaces, in the uniformly ionized

gas of the arc, become charged 5 to 15 volts negatively with respect to the gas. The wall of the tube thus absorbs all positive ions moving towards it, but repels all but a minute fraction of the electrons, so that these act largely as if specularly reflected from the wall without loss of energy or momentum.

The impact of the positive ions on the wall causes a heating effect on the wall which ranges from 15 to 50 per cent. of the total energy in the positive column.

The momentum delivered to the wall by the ions is the probable cause of the pressure effect observed by Hamburger and Skaupy by which the pressure of the gas near the anode is greater than at the cathode. Equations are derived by which this pressure effect may be calculated. The results are in rough agreement with the meager experimental data available.

Two methods are described for measuring the space potential in ionized gases. The first consists in the use of a hot sounding electrode whose potential is adjusted until the electrons emitted by it are just able to escape. The second is based upon a kink observed in a semi-logarithmic plot of the current voltage curve of a cold sounding electrode, which occurs when the electrode reaches the same potential as the surrounding space.

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THE SCIENTIFIC APPLICATIONS OF RADIOTELEGRAPHY.*

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RADIOTELEGRAPHY is taking a more and more important place, not only among the various methods of transmission of human thought, but likewise among the processes of research and analysis, for which it can be employed to extend the field of scientific knowledge.

Its evolution and growth have been extraordinarily rapid. It was first applied to intercommunication between ships at sea and the shore. Later, its introduction, in competition with land and cable lines, was attempted. The first efforts in this direction presented many obstacles, because at that time the technic of the art was undeveloped, and it may be truly said that if radiotelegraphy had been invented first, wire telegraphy would have been considered an immense improvement. It was the persistent work of a great number of physicists and engineers that little by little brought about such advances in the art, that to-day radiotelegraphy may be regarded as a powerful rival to the cable system. These advances have even made it possible, within a short time, for Hertzian telegraphy to make an invasion in wired telegraphy's own domain, and already "wired wireless" has received important applications, of which the final development is still far off.

Radiotelephony, in the meantime, had come into being, but its development is still very slow because of its many defects. However, even telephony by wire has scarcely attained a satisfactory degree of refinement. Despite the serious difficulties which Hertzian telegraphy and telephony still encounter in these different spheres, their future is assured, for new discoveries are constantly yielding important improvements.

It was soon realized that the transmission of radiotelegraphic and radiotelephonic messages were not the only useful applications of Hertzian impulses. Another class of practical application was

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evolved for the transmission of special signals. For instance, radiogoniometry, telemechanics, the reproduction of drawings, the piloting of airships by Hertzian impulses transmitted on telegraphic lines, etc. Many achievements of this kind are on record and the future is equally very promising in this direction.

It became finally possible to apply Hertzian waves, and their special technic to the study of purely scientific problems, and even to the creation of new methods of research in various branches of science.

To begin with, may be mentioned the considerable services rendered by Hertzian technic in a great number of questions relating to "time." While moderately precise hourly radio-telegraphic signals are a great aid to navigators in determining their position at a given moment, hourly signals of very great precision, with the aid of astronomic observations, permit this determination with a degree of precision unobtainable by any other process, where the error is of the order of ten metres. It was by this means that the difference in longitude between the observatories of Paris and Washington was determined in 1913. A very great number of analogous determinations have been made in all parts of the world by this method which has now become classic.

Under the direction of a special committee appointed by the International Unions of Astronomy and Geodesy, an international operation of this kind is in progress. The object is a redetermination, by this method, in coöperation, of the principal geographic points of the world with the greatest degree of precision attainable. One of the projects in view consists in determining, first of all, the position of three equidistant points and situated approximately on the same parallel at some medium latitude, such as San Francisco, Algiers and Shanghai. The sum of the three differences of longitude between these successive pairs of points should be 360 degrees. The departure from this figure will determine the value of the precision actually obtained. Without entering into the details of the project, it is interesting to point out that in the operation, new processes and highly perfected apparatus will be employed, as well for the astronomical observations as for the radiotelegraphic operations. A first series of preliminary observations, with the object of checking the methods and calibrat-

ing apparatus, is likely to be made at the end of the present year or in 1924.

If the precision with which the relative positions determined is only a few metres, as it is hoped, it will be possible, in repeating the operations several years later, to be assured that these relative positions have not changed, taking into account the displacement of the pole. If otherwise, the difference observed would be attributable to a deformation of the earth's crust, and a methodical study of that subject might then be undertaken.

In operations of the kind just outlined, it is necessary to know as nearly exactly as possible, the velocity of propagation of Hertzian waves on the surface of the earth. Already it has been shown that this velocity differs very little from the velocity of light. New measurements are shortly to be undertaken to increase the precision of this determination. Will it be possible to devise a method by means of Hertzian waves, leading to a repetition of an experiment analogous to that of Michelson? That appears very difficult, but not absolutely impossible. With the Dufour cathodic oscillograph, it is possible to measure practically, on a photographic plate, intervals of time of the order of the twenty millionth of a second, perhaps even a hundred millionth, counted on the record made by Hertzian waves. It may be possible to devise a method of utilizing this marvelous apparatus for the problem in view.

Still on the subject of "time," we may again call attention to the value of Hertzian impulses in investigations on the variation of the intensity of gravity at a given station at different times or at several stations at the same instant. The process is in effect a comparison of the periods of free pendulums at these points, that is to say, a comparison of the number of oscillations of these pendulums during a given time. This comparison is easily effected by inscribing at each station on the same recorder the oscillations of the pendulum and two Hertzian signals at an interval of several minutes which appear at all the stations.

It has even been possible for Mr. H. Abraham to contrive, by means of three-electrode tubes (audions or triodes) used in wireless telegraphy, a kind of clock which is entirely electric and devoid of any mechanical element, capable of producing electric "ticks" of extremely short duration at rigorously equal intervals and adjustable at will. By means of such "ticks"

the intervals of time, measured from any origin, registered in the determinations above mentioned, can be subdivided with all necessary precision. Perhaps we may contemplate, in the not too distant future, the employment of these electric clocks in place of the astronomical clocks now used, for these would not be subject, like the latter, to errors and variations due to mechanical causes, seismological, *et cetera*.

Astronomy is even further indebted to the development of Hertzian science. In judiciously combining radiotelegraphic amplifiers with potassium photo-electric cells, it is possible to record luminous signals in the same manner as electric signals. The measurement of the luminosity of stars can then be realized. For example, by simultaneously recording the trajectory of a star in the field of an equatorial telescope and the beats of the astronomical clock, it may perhaps be possible, during the time, to determine precisely the position from the points of the curve which correspond to the passages of the star behind the wires of the reticule. The personal influence of the observer will thus be eliminated and with it a serious source of error. This combination of photo-electric cells and radiotelegraphic apparatus will certainly develop many scientific and practical applications. Will it perhaps lead to a solution of the problem of electrical vision at a distance?

The phenomena of the propagation of waves in air, in water, in the ground, considered either separately or simultaneously with material vibratory movements, have also either made possible or indicated interesting solutions of a variety of problems. In effecting, for example, by means of radiotelegraphic devices, vibratory movements of high frequency, Mr. Langevin has succeeded in producing under water, ultra-audible pencils of rays which could be directed at will and which were reflected from objects in their path. A method of making soundings at sea of very great precision is a notable application of this phenomenon.

It may incidentally be mentioned that it has likewise been possible to measure the velocity of sound in water with very great precision, by the following method: An explosion in the water and a Hertzian signal are simultaneously produced at a given station. At another station, a microphone receives the sound impulse and an antenna the Hertzian signal. Both impulses are

recorded on the same chronograph and the difference of time indicated determines the velocity.

Other investigations are in progress for applying the propagation of high-frequency oscillations to the study of the nature and disposition of geological strata. Already interesting results have been obtained.

The propagation of Hertzian waves through the air is affected by a multiplicity of phenomena and the study of their anomalies has already resulted in much work in the analysis of certain of these phenomena which still remain puzzling enough. A notable one of these is that the energy proceeding from a given emission and received at some other point varies within very wide limits, with different days and with different hours of the day. The influence of the seasons and of solar light has also been definitely established. Moreover, when an emission is observed by means of a radiogoniometer, the direction indicated by this apparatus is not constant; it varies according to the hour of the day, and in a different manner in the various seasons, and particularly during the night. It has also been noticed that the variations observed from the same emission are not alike when the operators occupy different positions; they are likewise a function of the wave-length employed in the emission. Finally, atmospheric electric phenomena, as well as other not easily defined causes, introduce disturbances of reception by the superposition of these transient signals upon the normal radiotelegraphic signals. A critical study of all these facts has been in progress for several years, notably by Mr. Austin in the United States, by Messrs. Jouaust, Mesny and others in France, England and Italy. Numerous observations have been made each day, curves have been plotted, but no law applicable to all the facts has yet been disclosed.

Some generalizations, however, appear warranted at the present moment. For what applies to the mean value of the energy proceeding from a given discharge and received at a station, the Austin-Cohen formulas agree best with the actual results. On the other hand, the theoretic formulas by such mathematicians as Henri Poincaré, Macdonald, Nicholson, in the derivation of which they uniformly took into account the diffraction of the waves on the surface of the terrestrial sphere, did not account for the very considerable increase in range obtained in telegraphic transmission. Quite recently Mr. Watson has shown that in admitting, within

the limit of the atmospheric height of one hundred kilometres, the existence of a conducting stratum and consequently capable of reflecting the waves, the theoretic formula becomes identical with the Austin-Cohen formula. The existence of this stratum, the Heaviside layer, appears, moreover, to be justified by numerous considerations relating to astronomical physics. However, the Austin-Cohen formula only agrees with actual results with a rather wide approximation. It still remains to explain the variations of intensity of reception at the various hours of the day, radiometric deviations, . . .

Thus, the conclusion has been reached that the surface of the Heaviside layer was irregular, that certain phenomena of ionization which occurred beneath this layer in the upper atmosphere affected the propagation of the waves. Perhaps, indeed, it will be necessary to consider phenomena in even lower strata of the atmospheric layer. All this is still quite vague, but it can be scarcely otherwise, because we are unacquainted with nearly all the meteorologic and electric phenomena of the atmosphere. The numerous observations which are being made on the intensity and direction of radiotelegraphic reception will probably enable us to penetrate little by little into the mysteries of these phenomena. The waves which are observed, in effect, traverse all atmospheric regions situated between the points of emission and reception and consequently can throw light on the states of these regions. Meteorological stations are all keenly interested in these investigations and lend a most valued coöperation to radiographic physicists.

By the employment of very short waves, American and European radio amateurs have recently carried on with success some experiments in transatlantic communication, with apparatus of very low power. Numerous radio messages by telegraphy, and even by telephony, were obtained from both shores across the ocean. What path did these waves follow? Did they glide along the surface of the sea, or were they reflected by the Heaviside layer? It is yet impossible to conclude definitely. The very great irregularity of reception is not conducive to a ready solution; it demonstrates, however, that the atmosphere plays a dominant rôle in this matter. Special investigations are now in progress in France with a view to adding a new contribution to this research. By means of special antennæ, producing an adjustable directive

radiation, very short waves are transmitted on days and at hours announced in advance. Observations are made at various distances and already very interesting results have been obtained, notwithstanding that they are still insufficient to permit conclusions to be drawn from them.

Researches relating to the electric disturbances which affect receivers are likewise being carried on assiduously. Important observations have already been made, notably by Mr. Austin, concerning the direction of the source of these disturbances, but our knowledge on the subject of their nature and their various causes is still very imperfect. Researches and special experiments on these various questions have been undertaken by L'Union Internationale de Radiotélégraphie Scientifique, and it is to be hoped that in a few years it will be able to report substantial results.

In a different field, the development of Hertzian technic has considerably improved the precision and increased the variety of methods of electric measurements: Capacitance, inductance, resistance, specific inductive capacity, etc. The measurements of frequency, electromotive force, phase, etc., have equally been carried to a degree of precision previously unattainable. With respect to measurements of frequency, it is likewise notable that it will shortly be possible to control the frequency of a transmitter by means of the standard apparatus itself. This prospect will insure the attainment, on questions of frequency employed in practice, of an agreement very difficult to attain with other physical magnitudes.

It has been possible to extend the study of the magnetic properties of iron by making use of currents of very high and adjustable frequency, and by employing the devices of radiotelegraphic technic. The application of waves of very short length may possibly lead to a determination of the periods of vibration of atoms. The application of amplifiers has already made it possible to determine the appreciable time occupied by the molecules of iron in acquiring magnetization. It is also with this apparatus that Mr. Hollweck has rendered audible the emission of alpha particles. Measurements of the terrestrial magnetic field, moreover, can very easily be made by means of a new method evolved by Mr. Perot which again admits the employment of certain apparatus utilized in radiotelegraphy.

Even in medicine the progress of Hertzian technic has found very useful applications.

With electric furnaces, designed in accordance with the same principles, enormous temperatures have been realized which had never been obtained by previous processes.

It would be possible to cite many other researches and scientific work undertaken, in which either radiotelegraphy itself or methods and apparatus evolved for it are utilized. It is hence obvious that there is a boundless future for the applications of Hertzian waves and that it is to the greatest advantage of all physicists, whatever their specialty, to keep in close touch and coöperate in the development of this branch of science.

Antifriction Effect of Grooves in Bearings.—The settlement of the long-vexed question, grooves in bearings for efficient lubrication, may now be regarded as reached. Dr. T. E. Stanton, F.R.S., D.Sc., Director of the National Physical Laboratory, England, has just reported the result of his painstaking researches in a lecture, "The Nature of Lubrication in Engineering Practice," to the International Air Congress in London.

Doctor Stanton states as a result of his research that: "Using an ungrooved journal and an ungrooved bearing, with castor oil as the lubricant, it was found that steady conditions could be obtained, but that the coefficient of friction was 15 per cent. higher than with the grooved surfaces and that substituting a grooved journal for the plain one did not improve matters. In the case of the Bayonne oil the increase in friction due to using ungrooved surfaces was 22 per cent.

"It is clear, therefore, that a system of grooving is essential in order to obtain the minimum friction due to the materials of the surfaces and lubricant employed."

Particular stress was laid on the value of adding small quantities of organic acid to mineral lubricating oils, on which phase of the question *The Engineer* of London comments: "The insufficiency of the Reynolds theory is, however, in our opinion, presented by the known effect of adding small quantities of fatty acid to mineral lubricating oils. According to the hydro-dynamical view, the nature of the lubricant is immaterial, its viscosity alone affecting the result. Yet to take some figures recorded by Doctor Stanton, figures which are amply borne out by practical experience, the addition of 1 per cent. of organic acid to Bayonne oil, an amount quite insufficient to have any noticeable effect on the viscosity, reduced the coefficient of friction in a bearing by no less than 17 per cent."

H. L.

EFFECT OF THE GAUZE IN THE FRANCK MODIFICATION OF THE RUTHERFORD ALTERNATING CURRENT METHOD FOR MEASURING IONIC MOBILITIES.*

BY

LEONARD B. LOEB, Ph.D.

National Research Fellowship, University of Chicago.

IN a previous paper¹ it was shown that the apparent mobility of the negative ions, as given by the Franck modification of the Rutherford alternating current method, varied through large limits as the auxiliary field strength G was varied. It was further shown that the magnitude of this effect indicated rather an instrumental effect of the gauze than a change in the nature of the ion with time. It is the purpose of this paper to show just how this instrumental effect of the gauze must change the value of the mobility found by its use. An extensive series of measurements was made on the mobilities of the ions changing the values of the auxiliary field G (Fig. 4), the value of the alternating field at which the ions just cross E_0 , and the frequency of the alternating field, but maintaining all the other conditions the same. The gauze used was a perforated sheet brass .035 cm. in thickness and 10 cm. in diameter with 9 holes of 2.3 mm. diameter per square cm. Its distance from the plate p was 1.29 cm. and its distance from c was 1.42 cm. The frequencies used lay between 15 alternations and 75 alternations per second. The results obtained may be summarized as follows:

1. For $E_0/G = A$ less than unity the mobility of the ions lies above 2.15 cm./sec. and increases slowly as A is decreased to a value of 2.35 cm./sec. at $A = .08$.

2. For A greater than unity the mobility lies below 2.15 and decreases almost linearly as $\log_{10} A$ increases down to a value of 1.66 at $A = 55.0$.

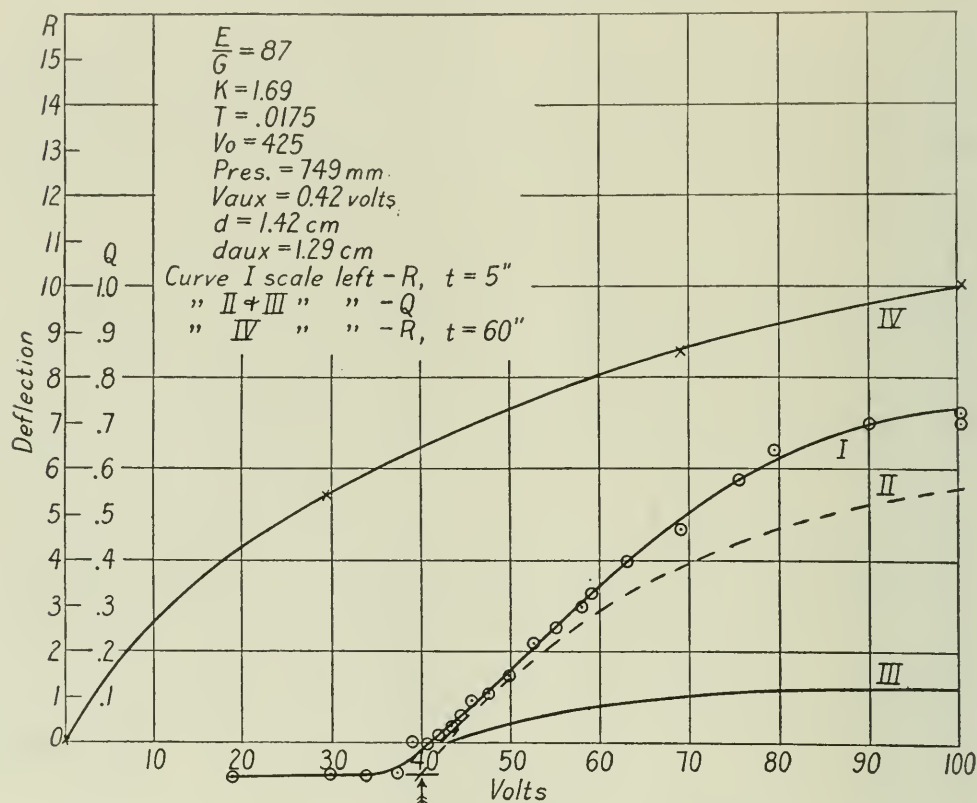
3. At values of A about unity the mobility curves make sharp intercepts with the voltage axis. As A decreases they remain fairly well defined except at the lowest values of A used, where

* Communicated by Dr. W. F. G. Swann, Associate Editor of this JOURNAL.

there is a distinct tendency for these intercepts to develop asymptotic feet. As A increases the intercepts become rapidly more and more rounded until at the point where $A = 55$ it becomes almost impossible to pick a definite intercept of the mobility curve with the axis (Figs. 1, 2 and 3, curves I).

4. For high values of G the current does not fall to 0 below E_0 , the critical value of the alternating field, but attains a constant

FIG. 1.



value equal to the current observed when E is 0 (Fig. 3). The magnitude of this current increases as G increases.

5. For lower values of G the ion current falls to 0 below E_0 and remains there (Fig. 2). At the lowest values of G the current below E_0 reverses in sign and increases in magnitude as G decreases (Fig. 1). The reversed current is in all cases small compared to the currents in the opposite direction observed with a large G .

6. If it be assumed that the ions have a unique mobility K and that all the ions start at the level of the gauze, *i.e.*, at a plane d cm. from the electrometer plate e , then the ions will reach the

upper plate in the time t if $t > d/EK$. If we designate the maximum possible current to the electrometer plate at a fixed field strength E as I_0 , then in a time dt the electrometer receives a charge $dq = I_0 dt$. For a square wave alternating field of strength E the ions can only cross during a time interval whose length extends from $t = d/EK$ to $t = T$, the time of an alternation, hence the quantity received by the electrometer in one alternation (*i.e.*, in a time T) is given by

$$Q = I_0 \int_{d/EK}^T dt = I_0 (T - d/EK)$$

Q can also be considered as the quantity delivered by an average current I , in a time T , hence

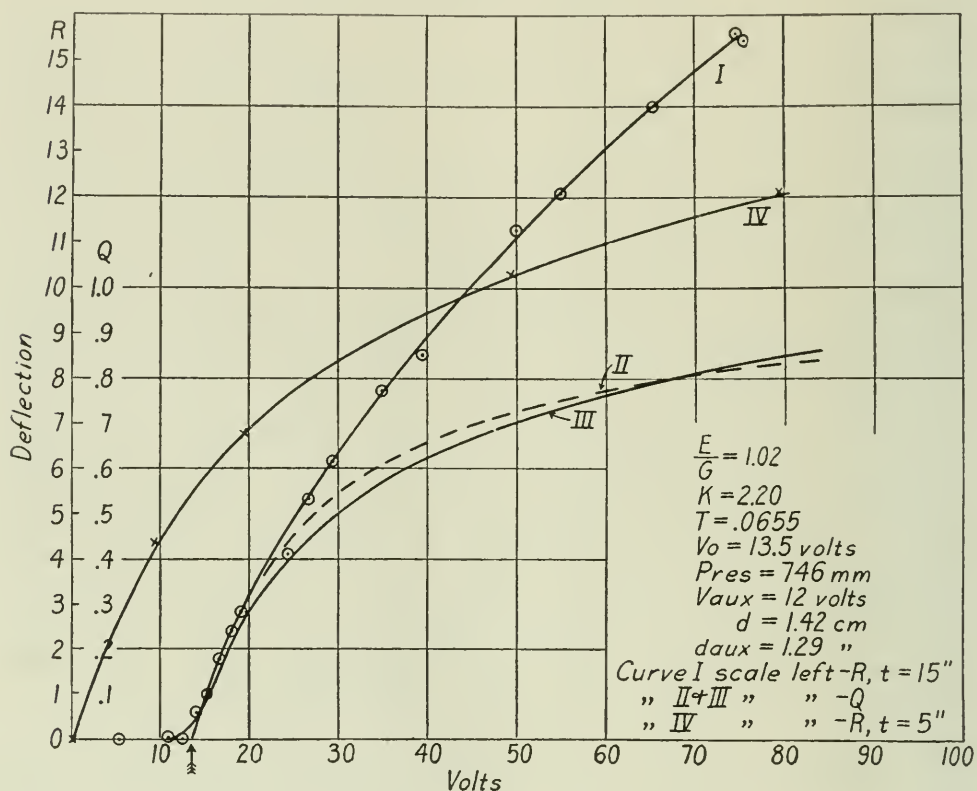
$Q = IT = I_0 (T - d/EK)$ or $I/I_0 = 1 - d/(TKE)$. But $d/KT = E_0$ where E_0 is the critical field strength for which ions can just cross the plates whence $I/I_0 = \frac{E - E_0}{E}$. Now experimentally I

is nothing but the electrometer reading at the alternating field strength E , and I_0 is one-half the maximum deflection possible for a field strength E when there is no alternating field, *i.e.*, it is the value of the saturation current. The reason that I_0 is one-half the maximum deflection with the fixed field, is that with the alternating field the ions are driven across the plate for but half the time, that they are with the fixed field owing to the reversal of the field. Now it was found on comparing the computed and observed I/I_0 curves for different values of A , that for values of A greater than unity the observed curves fell markedly below the computed ones, while for values of A below unity the two curves coincided in a satisfactory manner except for the lowest values attained where the observed curves rose very slightly above the computed ones. This is well shown in Figs. 1, 2 and 3 for values of A equal to 87, 1.0 and .068, respectively.

(In these figures curve III is the observed $\frac{I}{I_0}$ curve, curve II the computed one and I gives I while IV is the saturation curve.) In the extreme case of $A = 87$ the observed I/I_0 is only one-third the computed curve. This can mean only one thing under these circumstances and that is that with the relatively high alternating field only a fraction of the ions that are available reach the field E , and hence the upper plate.

To explain all these effects one need merely assume that a phenomenon occurs which has been found to occur in the use of gauzes or grids in other experiments, *viz.*, the penetration of fields through the gauze. It has been shown by Van der Bijl² and others that when we have a field G produced below a gauze as in Fig. 4a, it penetrates through the gauze to a slight extent, so that the field in the space labelled E above the gauze has no longer the value E indicated by the potential difference imposed upon

FIG. 2.



g and e , but attains a value $E + G/m$, where m is a quantity greater than unity and called by Van der Bijl the amplifying factor. The condition represented in Fig. 4a is the condition existing when the gauze g is in the negative phase of the alternating potential, *i.e.*, when ions are being driven to the electrometer plate E . When the field reverses in E , as in Fig. 4b, then the field G still attempts to penetrate the gauze in the same sense as before. However, the field in E also acts to penetrate the gauze in the opposing sense. The resulting field will be determined by the relative strengths of the fields G and E .

Let us assume that $A = \frac{E_0}{G}$ is less than unity. Then the field driving the ions to the electrometer plate c is actually $E + G/m$, while in computing the mobility the field is assumed to be E . Thus since K is taken as $d/\bar{E}T$, K will appear larger than it really is. In fact K' , the erroneous value of the mobility, will be related to K the true value, by $K'/K = \frac{d/E_0T}{d/(E_0 + \frac{G}{m})T} = 1 + 1/Am$. If the

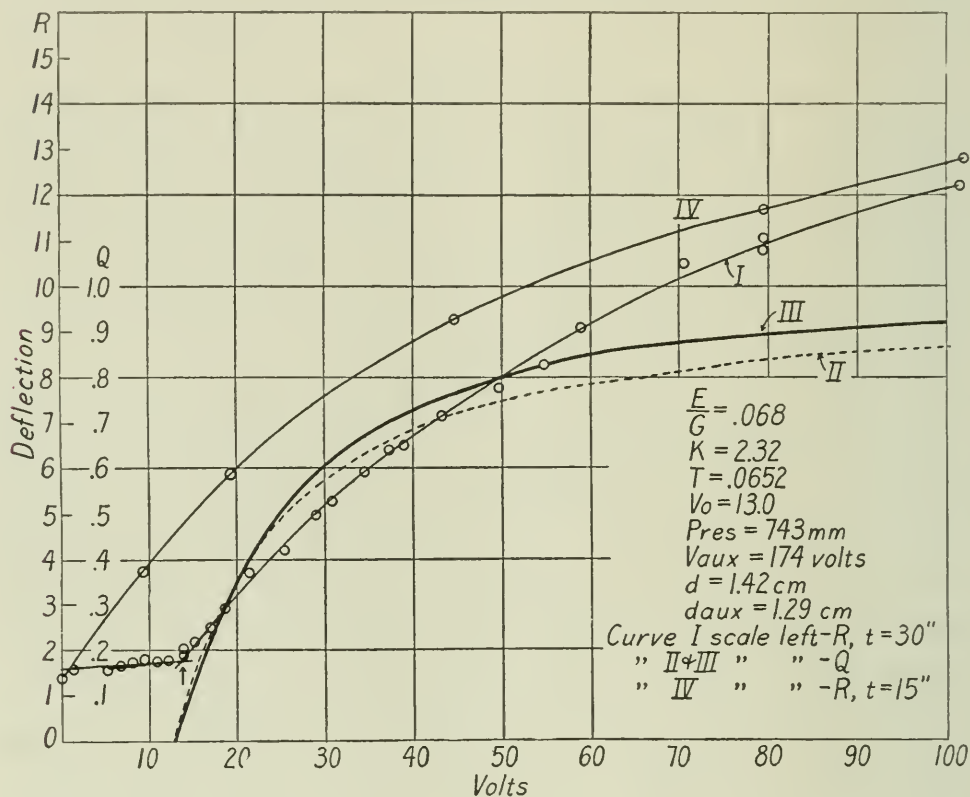
quantity m^\dagger has a value of about 200, which is not an unreasonable assumption, $K'/K = 1 + \frac{1}{.07 \times 200} = 1.07$ for the case where A is .07. This increase in K is of the same order of magnitude as that which was actually experimentally observed, for this value of A . A closer verification of this relation experimentally is impossible on account of the erratic variations of the values of the mobility produced by the conditions of measurement. It is obvious from the equation that as A increases the apparent mobility will decrease to nearly the normal value at $A = 1$.

In general for A equal to unity the ions will start from the level of the gauze at the opening of the negative phase, for in the preceding positive phase the two penetrating fields in opposite directions essentially neutralize each other, and so ions cannot penetrate into the field E . As A decreases, however, the field penetrating from G will predominate and at the beginning of the negative phase some ions will find themselves above the gauze. In general the number accumulating will be small as the fields are so intense as to carry most of the ions to the gauze. Thus one would expect that near $A = 1$ the intercepts of the mobility curves would be sharp and the theoretical I/I_0 curves would coincide with the computed ones (curves II and III, Fig. 2). For very low values of A the ions would not start at the level of the gauze but slightly above it, and this small accumulation of ions above the gauze would contribute more to the current than theory calls for, since they enter the space before the negative phase begins. Thus the observed I/I_0 values would

[†] An attempt at the direct evaluation of m for the conditions of these measurements was made and gave $m = 130$. This can, however, only be taken as the lower limit for m as the value is exceptionally sensitive to improper electrostatic shielding and it is almost impossible to decide when this has been achieved.

be slightly greater than the computed ones (curves II and III, Fig. 3). The intercepts of the mobility curves would also tend to become less definite because of the indefinite level from which such accumulated ions start. As can be seen in Fig. 3, this actually occurs. Finally, if the field E be made 0, since the penetration of the field G gives an effective field G/m between g and e , there should be an appreciable current to the electrometer

FIG. 3.

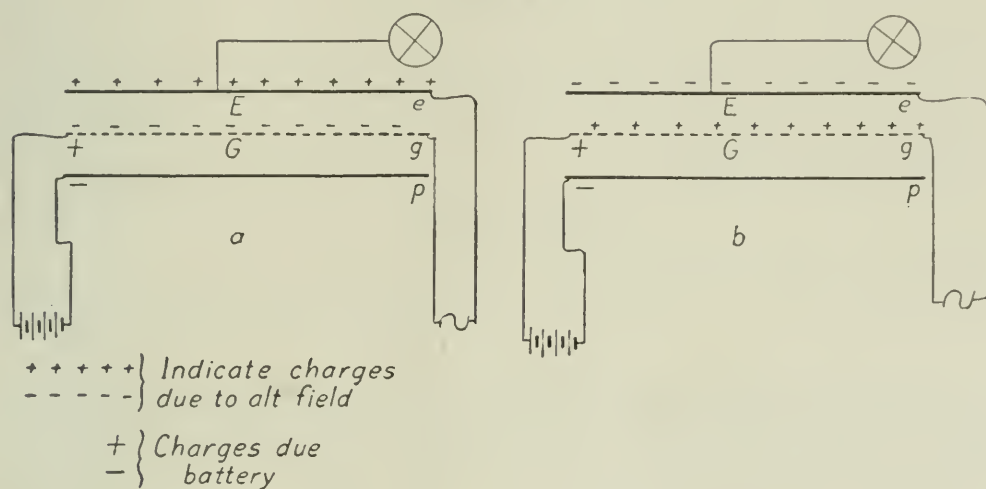


due to this field. The existence of the penetrating field is definitely shown by the constant electrometer current below the critical value E_0 (Fig. 3). The magnitude of this current is about that which would be expected from a field of $G/100$ volts/cm.

Let us now take A greater than unity. Under these circumstances the effect of $G/200$ on E in the negative phase becomes entirely negligible. During the positive phase of E , however, the field E/m penetrating the gauze in a sense opposite to G becomes appreciable. In the case where $A = 55$, E/m becomes about 0.3 volt per cm., while the value of G is actually but 1.16 volts/cm. Thus, in the neighborhood of the meshes, the ions encounter a

retarding field which keeps them from entering E . As a result of this the ions are driven by the opposing fields to the metal gauze where they are lost. Accordingly, at the beginning of the negative phase there is below each mesh of the gauze a small space, which might achieve a depth of 2 mm., in which no ions are to be found, and the depth of this space will increase as A increases. Thus an appreciable period will elapse before the ions are driven across the space into the field in E , with the weak field existing in G . This delay will act to shorten the effective value of T the time of action of the alternating potential, a stronger E_0 will be required to force them across in this time, and hence the value of the mobility will

FIG. 4.



appear too low. An exact evaluation of the magnitude of this effect is not easily accomplished. The production of these ionless pockets below the meshes of the gauze will have for a result that the starting level of the ions at the initiation of the negative phase will be far less clearly defined than before, so that the mobility curves should develop markedly asymptotic intercepts with the voltage axis as A increases (Fig. 1). The loss of the ions from the region of the pockets will also have the effect of reducing the total number of ions available for the electrometer current. Thus the observed I/I_0 curves should fall below the computed curves, as is actually seen to be the case in curves II and III, Fig. 1. Finally, if the field due to E during the negative phase is great enough it may succeed in pulling a few positive ions from the space C during this phase and hence produce a reversal of the current. This would become manifest especially below E_0 where no nega-

tive ions were crossing, since the positive phase of E was always greater than the negative phase by about 10 per cent.

It is therefore seen that all the phenomena connected with the change in K produced by varying the auxiliary field can be satisfactorily accounted for by the penetration of the fields through the gauze, so that no necessity arises for calling upon vague speculations as to ion formation to account for the phenomena. It may be pointed out that when the value of A approaches unity the conditions are essentially fulfilled for determining the true value of the mobility of the negative ions, for under these circumstances the computed and observed I/I_0 curves coincide. The value of the negative ion mobility obtained at this point lies close to 2.20 cm./sec., which agrees with the value found for the negative ions without the use of the gauze in the preceding paper.

In conclusion the writer wishes to acknowledge his thanks to Prof. W. F. G. Swann for his kind advice and criticism in the writing of this paper.

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¹ LOEB, L. B.: This JOURNAL, October, 1923, p. 537.

² VAN DER BIJL, H. J.: "Thermionic Vacuum Tube," McGraw Hill, 1920.

Corrosion of Industrial Metals.—In a conference of members of the Faraday Society and the Sheffield Section of the Institute of Metals much information was presented concerning the corrosion of common metals and alloys. Dr. D. W. Hatfield, of Sheffield, gave a summary of his experiments and observations on the corrosion of industrial metals, including forms of iron and steel, silicon iron, aluminum, duralumin, and several kinds of bronzes. Tests were made with mineral and vegetable acids, fresh and sea water and some common salts. Contrary to what might be expected from the electrochemical theory, some of the heterogeneous alloys, such as nichrome, stainless steel and silicon iron, showed the most resistance. Aluminum and monel metal show resistance, but Doctor Hatfield regards them as essentially heterogeneous owing to impurities. Steel containing 14 per cent. of manganese is very soluble in acids, and is also subject to general corrosion. As a result of extended experiment, Doctor Hatfield is led to the following views: Alloys and steels are now available that effectively resist corroding influences. Actual test representing the conditions to which the material is to be exposed must be made in each case. No law is yet elucidated which enables the metallurgist to foretell the action of a given corrosive agent on a given metal or alloy. In the paper, considerable attention is given to the physical chemistry of the subject.

H. L.

STUDIES IN PHOTOGRAPHIC SENSITIVITY.*

III.

TOPOCHEMISTRY OF DEVELOPMENT AND SENSITIZING NUCLEI.

BY

S. E. SHEPPARD, E. P. WIGHTMAN AND A. P. H. TRIVELLI.

Research Laboratory of the Eastman Kodak Company.

VIII. DESTRUCTION AND REGENERATION OF LATENT IMAGE AND THE EFFECT OF KI.

I. *Physical Development before Fixation and Chemical Development.*—We now proceed to the action of potassium iodide, in conjunction with chromic acid, on the *latent image*, both for physical development before fixation, and chemical development. In Table IX (see this JOURNAL, preceding number) are given some results with quite weak CrO_3 solutions, and 1 per cent. iodide. From these it appears:

(a) With physical development of Graflex emulsion only 16° C.J. were obtained, as against 25° by chemical development.⁴⁴ But, using a bath of 1 per cent. iodide after exposure, with 5 per cent. Na_2SO_3 (to reduce oxidation, according to Lüppo-Cramer) 22° C.J. were obtained by physical development, 23° C.J. by chemical. This is a much closer approximation, and agrees with Lüppo-Cramer's results on the favoring influence of KI on physical development. But, before the whole of this be attributed to "nucleus exposure," note from Table IX, experiments 529–530, that on soaking in plain water before physical development, 20° C.J. are obtained instead of 16° . This difference between "dry" and "wet" plates was repeatedly confirmed, and shows that part only of the iodide effect is to be attributed to the iodide itself. Experiment 489,

* Communicated by Dr. C. E. K. Mees, Director of Laboratory and Associate Editor of this JOURNAL. Published as Communication No. 190 from the Research Laboratory of the Eastman Kodak Company. Concluded from JOUR. FRANK. INST., November, 1923. p. 673.

⁴⁴ Chapman-Jones values are only relative and not absolute.

Table IX, shows that quite dilute chromic acid after iodide cut back the scale to 15° for physical, but practically did not affect it for chemical development. This discrepancy again is not easy to account for on the "nucleus exposure" hypothesis as the results in the table show, the effect with physical development is lessened when there is Na_2SO_3 present with the KI. (Cf. also experiments 490 and 517.) The results with .05 per cent. CrO_3 are not very conclusive, and some further tests were made with .2 per cent. CrO_3 . Experiments 521 and 522 show that a repetition of $\text{CrO}_3 \rightarrow \text{KI}$ and of $\text{KI} \rightarrow \text{CrO}_3$ treatment gave very similar results for physical development. The image was not completely destroyed. This may be a question both of size of grain and thickness of emulsion layer. The experiments 525, 526, 508, 518 with CrO_3 alone, followed by Na_2SO_4 pickle, are not very concordant, which may be partly due to the circumstances already noted, but possibly also to the uncertainty of elimination of CrO_3 with the sulphate pickling bath.

(b) In regard to *chemical development*, experiments 503, 509, 510, 511, 512, the .05 per cent. CrO_3 , used for short times, was evidently little effective, but .20 per cent. lowered the scale from 25° to about 15° with iodide, to 19° without. Here again, the order $\text{CrO}_3 \rightarrow \text{KI}$ or $\text{KI} \rightarrow \text{CrO}_3$ gave much the same result.

Applying the same treatment to lantern slide emulsion, Table X shows the results in part. The experiments are not quite comparable with the Graflex ones, but indicate a lower resistance of the latent image. Experiment 419 showed a definite "revival" of the latent image for physical development, after destruction by CrO_3 , by use of .34 per cent. KI. With .05 per cent. CrO_3 and *chemical development*, inconclusive results were obtained, since, though plain CrO_3 gave loss of scale, .34 per cent. iodide *followed* by CrO_3 gave no loss, nor .34 per cent. iodide alone. Yet on the disinterment theory, the iodide pretreatment should have led to nearly total destruction. In one case of repeated $\text{CrO}_3 \rightarrow \text{KI} \rightarrow \text{CrO}_3$ treatment, reduction to 16° C.J. was effected, but this was not confirmed by the check experiment, which showed only slight loss of density.

These results require further work with higher CrO_3 strengths.

TABLE X.

Action of CrO₃ and KI on Latent Image. Seed Lantern Slide; Exposure 16 min. at 25 cm. From 5-volt lamp.

Expt.	Treatment.				Result in Degrees C. J.	
	1	2	3	4	Phys. Develop.	Chem. Develop.
414	Nil					
415	{ 0.5% CrO ₃ 0.12% H ₂ SO ₄ 5 min.	3 washes	{ 0.17% KI 2 min. }	Wash	> 25 0*	
416	{ 0.5% CrO ₃ 0.12% H ₂ SO ₄ 5 min.	3 washes	Wash		0	
<i>Exposure 4 min.</i>						
417	Nil				23	
418	As in 415	3 washes			0	
419	As in 415	3 washes	{ 0.34% KI 2 min. }		19	
420	As in 415	3 washes	{ 5% Na ₂ SO ₃ 2 min. }		0	
<i>Exposure 160 sec.</i>						
421	Nil					25
422	0.34% KI	Wash				25
423	0.34% KI	{ 0.05% CrO ₃ 5 min. }				
424	0.05% CrO ₃	Wash				20
<i>Exposure 3 min.</i>						
648	{ Wash 15 min.				24+	
649	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash			0	
650	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash	{ 0.17% KI 2 min. }	Wash 15 min.	13	
651	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash	{ 0.34% KI 2 min. }	Wash 15 min.	22	
652	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash	{ 1.0% KI 2 min. }	Wash 15 min.	20	

* Experiment 415 is not in agreement with experiments 419, 650, 651, 652, and 659, and appears to be an error in recording the experimental work or in the work itself.

TABLE X.—*Continued.*
Action of CrO₃ and KI on Latent Image. Seed Lantern Slide;
Exposure 3 min. at 25 cm.

Expt.	Treatment.				Result in Degrees C. J.	
	1	2	3	4	Phys. Develop.	Chem. Develop.
653	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash	0.34% KI	Repeated 1, 2, 3 and then wash 15 min.	0	
654	{ 0.34% KI 5% Na ₂ SO ₃	Wash 15 min.			24 +	
655	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash 15 min.	{ 0.34% KI 5% Na ₂ SO ₃	{ Wash 15 min. and then repeat 1 and wash again 15 min.	0	
657	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash 15 min.	{ 5% NaHSO ₃ 10 min.	Wash 15 min.	0	
658	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash 15 min.	5% Na ₂ SO ₃	Wash 15 min.	0	
659	{ 0.5% CrO ₃ 0.1% H ₂ SO ₄ 5 min.	Wash 15 min.	{ 1% KI 5% Na ₂ SO ₃	Wash 15 min.	20	

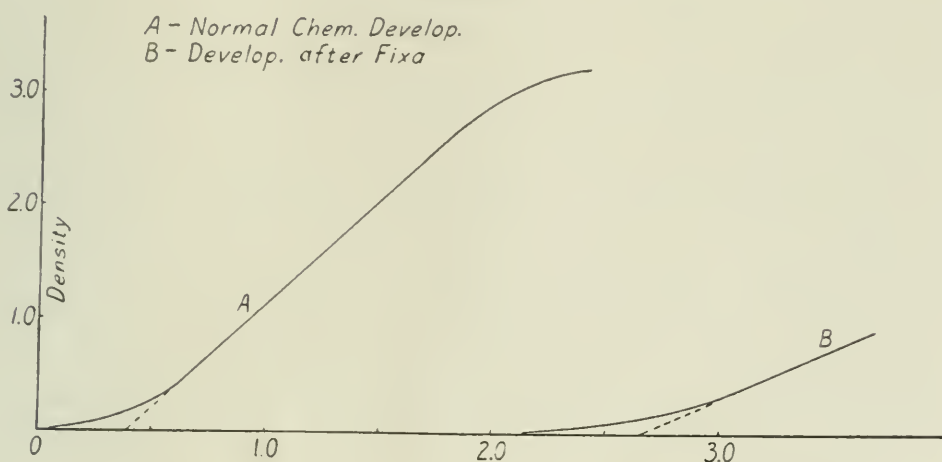
But they show that the effect of iodide in conjunction with oxidizers destroying the latent image is not as simple as represented by Lüppo-Cramer. On the other hand, the results with physical development, before fixation, on lantern plates (Table X) and with .5 per cent. chromic acid, are in good agreement with Lüppo-Cramer's theory. Regeneration, or "disinterment" of occluded latent image, after destruction of the "soluble" latent image with .5 per cent. CrO₃ is shown in experiments 649, 651, 652. A further treatment with CrO₃ destroys this, and still further treatment with KI is ineffective, as would be expected.

Part of the iodide effect here may be attributed to the increased adsorption by Ag-ions from the acid silver developer making a smaller, reduced nucleus more effective. Parallel experiments, so far as possible, with chemical development, are in hand, and should show whether the "disinterment" hypothesis is confirmed by this.

2. *Physical Development after Fixation.*—If the superficial

"latent image" be removed by chromic acid, the "occluded" image set free or disinterred by iodide, and this then removed by chromic acid, there should remain very little for development after fixation. Some preliminary experiments with lantern emulsion showed some reduction by such multiple treatment, but the chromic acid used was only .05 per cent. and the experiments will be extended with stronger solutions. As illustrating the range of "latent images" already referred to (p. 661 of previous paper), it required an exposure of 1920 seconds to give the

FIG. 2.



same "Schwellenwert" for development after fixation as 40 seconds did for normal chemical development. The comparison is illustrated by the characteristic curves in Fig. 2.

It is to be noted that in these experiments concentrations of KI of the order found effective in accelerating development with low potential developers⁴⁵ (Lainer effect) were used. *As a general result, such concentrations of iodide had little or no effect upon the action of oxidizing agents.* While the former is most effective at concentrations of the order of .002 to .02 per cent., the latter requires concentrations of the order .2 to 2 per cent. As we shall show later, the physical disintegration, and increase of surface, produced by the action of iodide on the original AgBr grain, increases very rapidly up to 1 per cent. KI.

So far as the effect of persulphate on the latent image and sensitivity is concerned, it appeared less effective, and much less reproducible, than chromic acid. Experiments made with 5 per

⁴⁵ Cf. Sheppard and Meyer, *loc. cit.*

TABLE XI.

*Action of Persulphate on Latent Image (a) and on Sensitivity (b).
Seed Graflex Plate.*

Expt.	Treatment.				Chemical Development Results in C. J.	
	1	2	3	4	(a)	(b)
109	Nil	Washed			24-5	24-5
121						
110	{ 2% $\text{Am}_2\text{S}_2\text{O}_8$ 0.5% H_2SO_4 5 min.	Washed			20	15
122						
111	{ 2% $\text{Am}_2\text{S}_2\text{O}_8$ 0.5% H_2SO_4 5 min.	Washed			20	
123						
113	{ 2% $\text{Am}_2\text{S}_2\text{O}_8$ 0.5% H_2SO_4 5 min.	Washed	5% Na_2SO_3	Washed	21	20
114						
124	{ 2% $\text{Am}_2\text{S}_2\text{O}_8$ 0.5% H_2SO_4 5 min.	1% Na_2SO_3	Washed		23	15
125						
139	{ 5% $\text{Am}_2\text{S}_2\text{O}_8$ 0.5% H_2SO_4 5 min.	Washed			15	14
140						
141	{ 5% $\text{Am}_2\text{S}_2\text{O}_8$ 1% H_2SO_4 5 min.	Washed			15	15
142						
144	{ 2% $\text{Am}_2\text{S}_2\text{O}_8$ 0.5% H_2SO_4 5 min.	Washed			17	
145						
146	{ N/5000 KI 2 min.	Washed	{ 2% $\text{Am}_2\text{S}_2\text{O}_8$ 0.5% H_2SO_4 5 min. 2% $\text{Am}_2\text{S}_2\text{O}_8$ 0.5% H_2SO_4 5 min.	Washed	19	15

cent. solution to find if prolongation over 10 minutes of the persulphate bath had any marked effect, showed no increased effect up to 140 minutes. A fogging action on unexposed halide, as previously recorded by Lüppo-Cramer, was frequently observed.

Experiments with a silver chloride emulsion showed a much greater resistance of the *latent image* to persulphate than the bromo-iodide emulsion. As in the case of chromic acid, the reduction of *sensitivity* by persulphate could be completely annulled by a bisulphite bath; both bisulphite, and still more neutral sulphite, producing increase on sensitivity.

IX. ON THE CONTINUITY OF SENSITIVITY, THE LATENT IMAGE, THE SOLARIZED LATENT IMAGE, AND THE VISIBLE IMAGE.

The great differences in behavior which naturally distinguish these phases of the photographic material (or better, define them) can very probably be explained in terms of the topochemical relations of colloid silver to grains of the silver halides, AgCl, AgBr, AgI, and their mixtures. Some reservation may be necessary with regard to sensitivity itself, which may not enter entirely into this category,⁴⁶ but with the other stages the evidence is fairly conclusive. The parallel behavior of "sensitivity" and "latent image" to oxidizers has already been noted here; the possibility of converting the solarized (reversing) plate into a sensitive plate has been frequently discussed. The use of oxidizers, such as persulphate, chromic acid, etc., in effecting this⁴⁷ indicates that excess "free" colloid silver can be removed by such oxidizers. Since a *reversed* image is obtained on re-exposure and development, the "occluded" image must still be affecting the process. On the other hand, after-treatment by such oxidizers, and development, without intermediate re-exposure to light, a *normal* image can be obtained, although development is very slow. We shall return to these "reversal" effects in a later communication, but may note here that Lüppo-Cramer⁴⁸ finds that a treatment with persulphate or chromic acid, which has the above-mentioned effect on the reactions of the solarized image, had no effect on the visible image, on such solarized plates. In partial agreement with this we found that impregnation of a Graflex plate with 1 per cent. CrO_3 did not affect appreciably

⁴⁶ The idea of sensitizers raises the issue whether they act by a preliminary formation of a trace of colloid silver, or whether the sensitizer and silver halide form a complex which is affected by light, *e.g.*, with reduction of the silver halide.

⁴⁷ Sterry, Lüppo-Cramer, Vidal, *et. al.* Cf. Lüppo-Cramer, *Photo. Prob.*, 1907, p. 112, 147, 190.

⁴⁸ *Phot. Korresp.*, 1902, p. 694; *cf.* also J. M. Eder, *ibid.*, p. 648.

the production of a visible image. Further, the action of 6 per cent. chromic acid in bleaching out the visible image was very slight on fast, coarse-grained emulsions. On others it was variable, depending upon *both* grain size and the composition, *i.e.*, proportions of iodide, bromide, and chloride (*cf.* Table XII).

TABLE XII.

Emulsion.	Composition.	Scale Reduction of Visible Image.	Color Change.
D. O. P. Paper	AgCl	18 12	Pink → Mauve
D. O. P. Papers	AgCl } AgBr }	18 10	
Bromide	AgBr	18 0	Pink White
Lantern	AgBr	18 10	Blue → Mauve
High Speed	AgBr } AgI }	18 18	Purple } → Gray gray }

These observations are noted for the sake of completeness, since they indicate the relative importance of the topochemical factor along the whole series of photographic phenomena.

Although straight chloride emulsions give high resistance, increase of bromide reduces it. But with a coarser grain, the bromide emulsions acquire a higher resistance again.

In general, our work fully confirms Lüppo-Cramer's general thesis of "facilitation of formation of free silver nuclei [germs] in consequence of the *presence* of silver iodide." We suggest that the reason for this lies in the lattice structure (arrangement of the atoms) of silver bromide and silver iodide, respectively. AgBr has a simple cubic structure,⁴⁹ of open type, in which solid solution of silver could occur relatively easily, *i.e.*, in terms of metallographic analysis, it is a good "host" to silver.⁵⁰ On the other hand, silver iodide forms naturally at these temperatures, a tetrahedral lattice of much more compact form, so that solid solution of silver would be precluded. It is this difference, we believe, together with the high adsorption of silver *ions*, etc., to silver iodide, rather than mechanical denudation which explains most of the remarkable iodide effects. Freshly formed silver—by exposure to light, or by development—is forced to orient itself differently, according as iodide is present or not.⁵¹

⁴⁹ R. B. Wilsey, *Phil. Mag.*, **42**, 262 (1921).

⁵⁰ *Cf.* W. Rosenhain, *Chem. Met. Eng.*, 1923, p. 442.

⁵¹ *Cf.* S. E. Sheppard, "Action of Soluble Iodides, Etc.," *loc. cit.*

X. THE INFLUENCE OF OXIDIZERS ON THE SENSITIVITY,
WITH ONE-GRAIN LAYERS.

In one-grain layers diffusion and strato-chemical effects are reduced to a minimum and may be regarded usually as negligible. The plates were prepared by a method already described by us.⁵²

FIG. 3.

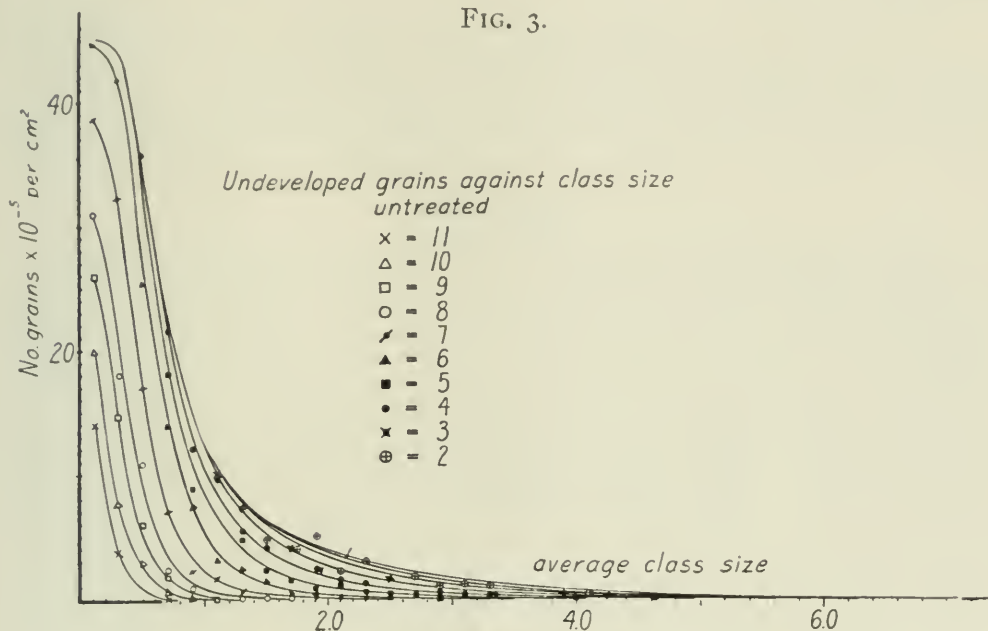
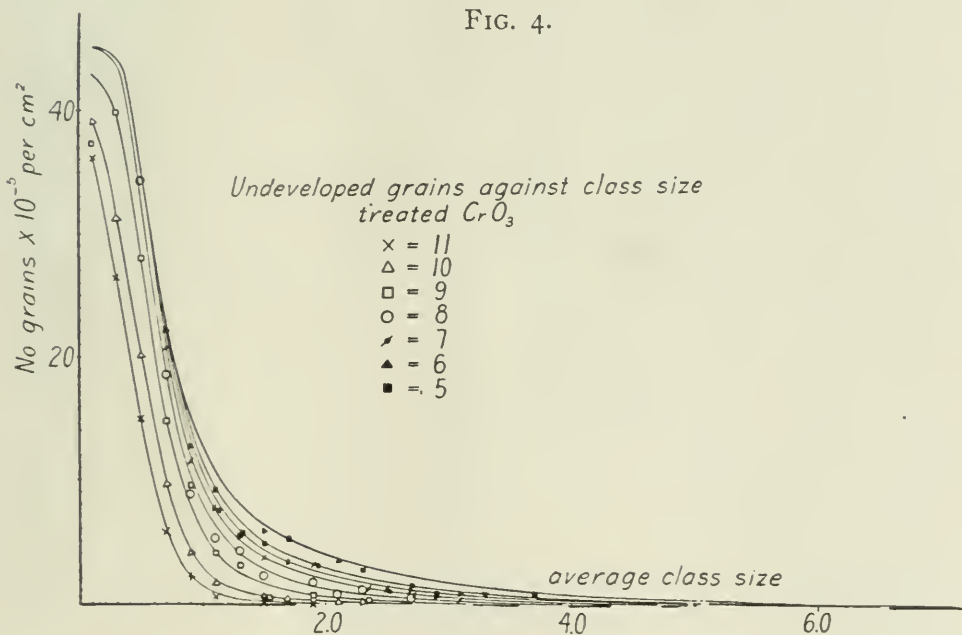


FIG. 4.



⁵² J. Phys. Chem., 27, 1 (1923).

removed with chromic acid mixture (.5 per cent. CrO_3 + .5 per cent. H_2SO_4), and photomicrographs made. Blank controls with the NaHCO_3 , etc., showed practically no difference from untreated plates. From the photomicrographs of the residual silver halide grains, size-frequency curves were constructed of the original and residual grains in different exposure steps.

Tables XIII and XIV give the frequency or distribution data of the residual grains. (Taken from the smoothed curves as illustrated in Figs. 3 and 4.)

TABLE XIV.

Graflex CrO₃ Treated. Residual Grains $\times 10^{-5}/\text{cm.}^2$ From Smooth Curves.

Class Size.	Original -Fog.	Steps 1 to 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10	Step 11
0.11	45.1	Too erratic to determine.	45.1	45.1	45.1	45.1	42.8	39.1	36.2
0.3	44.2		44.2	44.2	44.2	43.8	39.8	31.3	26.5
0.5	34.9		34.9	34.9	34.9	32.6	28.0	20.2	14.7
0.7	22.5		22.5	22.0	20.6	18.5	14.9	9.5	6.0
0.9	15.0		14.3	13.25	11.9	10.3	7.9	4.1	2.20
1.1	10.7		9.30	8.50	7.5	6.2	4.10	1.85	0.81
1.3	8.0		6.50	5.85	5.05	4.00	2.45	0.95	0.32
1.5	6.4		4.90	4.30	3.70	2.70	1.56	0.50	0.18
1.7	5.25		3.85	3.34	2.80	1.90	1.03	0.35	0.08
1.9	4.38		3.10	2.66	2.15	1.40	0.69	0.20	0.03
2.1	3.67		2.52	2.15	1.65	1.03	0.46	0.13	
2.3	3.13		2.09	1.74	1.31	0.76	0.30	0.08	
2.5	2.63		1.73	1.40	1.02	0.56	0.21	0.04	
2.7	2.22		1.43	1.12	0.81	0.41	0.13	0.02	
2.9	1.88		1.19	0.90	0.61	0.29	0.07	0.01	
3.1	1.60		0.99	0.73	0.48	0.20	0.04		
3.3	1.37		0.83	0.59	0.37	0.14	0.02		
3.5	1.15		0.68	0.47	0.28	0.09			
3.7	0.96		0.65	0.37	0.20	0.06			
3.9	0.80		0.48	0.30	0.15	0.03			
4.1	0.68		0.38	0.24	0.11	0.01			
4.3	0.59		0.32	0.20	0.080				
4.5	0.50		0.265	0.160	0.060				
4.7	0.42		0.215	0.115	0.040				
4.9	0.35		0.172	0.098	0.025				
5.1	0.29		0.138	0.073	0.015				
5.3	0.24		0.110	0.055	0.008				
5.5	0.20		0.090	0.040	0.002				
5.7	0.16		0.070	0.029					
5.9	0.13		0.055	0.020					
6.1	0.10		0.040	0.013					
6.3	0.08		0.031	0.009					
6.5	0.07		0.026	0.006					
6.7	0.06		0.021	0.004					
6.9	0.05		0.016	0.002					
7.1	0.04		0.010						

From the plotted data smoothed curves were drawn through the points, without attempting to fit an equation, since previous work had shown the Graflex emulsion to be unrepresentable by a simple equation. At this stage the "clumping" effect also was neglected. To obtain the distribution of the developed grains the

FIG. 5.

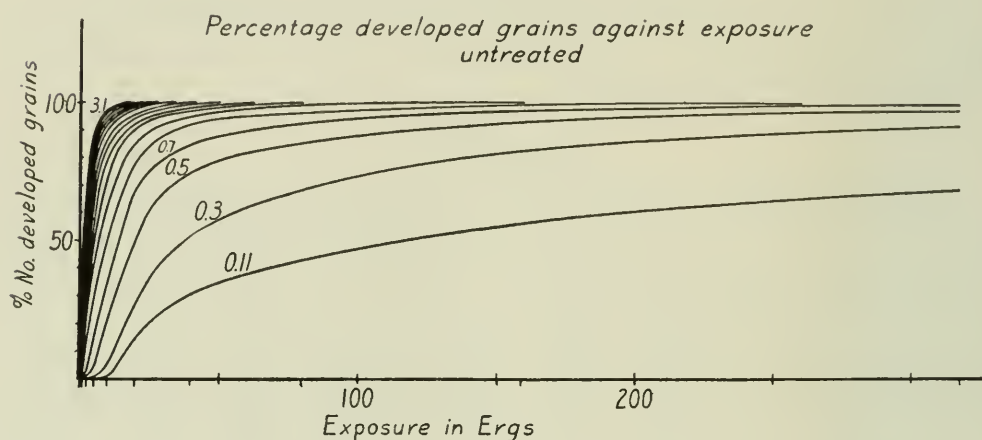
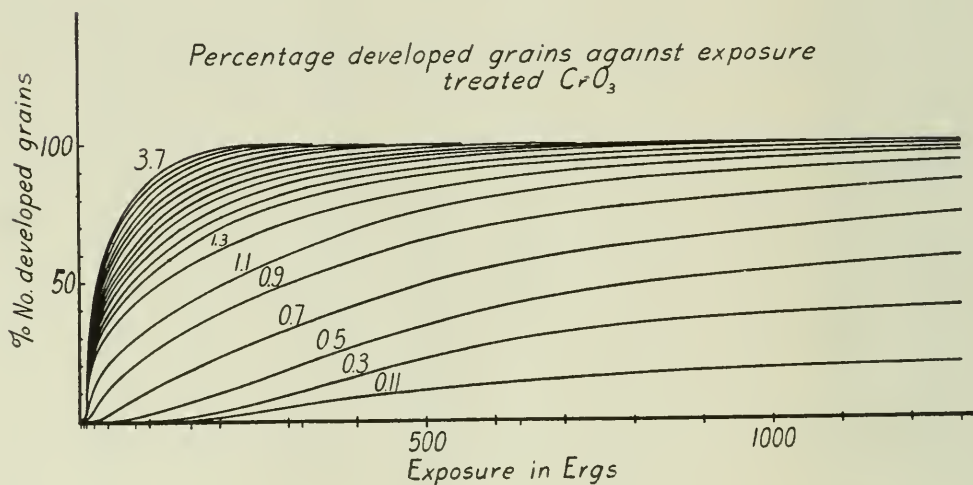


FIG. 6.



"residual" curves were subtracted from the original frequency curve, less "fog" which only amounted to about 3 per cent. of the number of grains.

Dividing the number of developed by that of the original grains in each class size the per cent. developed grains were

obtained. These values were plotted against grain size and against exposure. The results are given in Tables XV and XVI and Figs. 5, 6, 7 and 8.⁵³

FIG. 7.

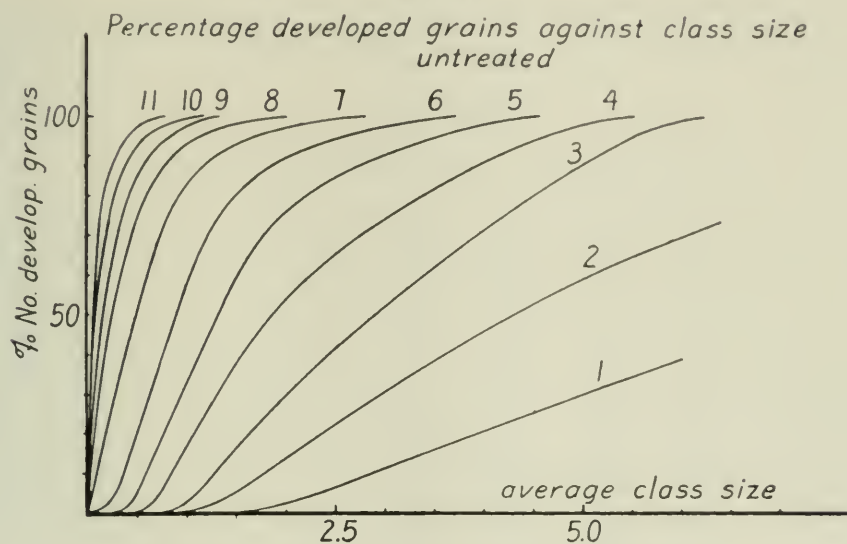
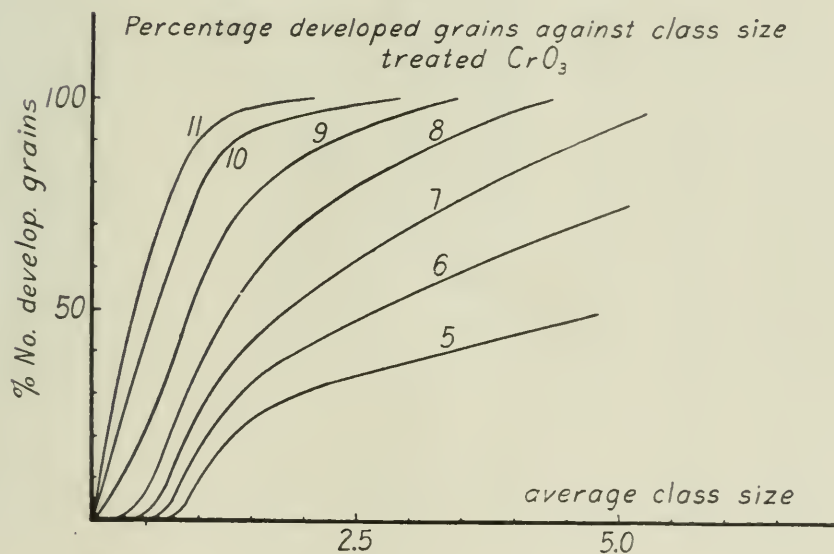


FIG. 8.



Furthermore, the ratios of untreated to treated grains for corresponding exposures are given in Table XVII.

⁵³ Values for the lowest exposures have been omitted, as the accuracy was quite small.

With some few exceptions, the ratios show a general decrease (towards unity as limit) with increasing grain size (and with increasing exposure). This means that the effect of chromic acid is greater on the small grains than on the large, but this selectivity is diminished as the absolute exposure is increased.

Some reversal of this effect appears to occur on passing to the

TABLE XV.

Graflex Untreated. Percentage Grains Developed.

Class Size.	Orig. Emul.	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10	Step 11
.11	100	0.	0.	0.	0.	0.	0.9	11.8	31.0	42.4	56.1	68.7
.3	100	0.	0.	0.	0.	0.	5.0	27.2	52.0	68.1	82.4	91.4
.5	100	0.	0.	0.	0.	4.0	22.6	51.0	74.8	85.1	92.5	97.4
.7	100	0.	0.	0.	4.0	17.3	34.7	68.4	84.9	92.4	96.9	99.6
.9	100	0.	0.	1.3	13.0	28.0	50.6	78.6	92.0	96.0	98.7	100.0
1.1	100	0.	0.9	5.6	21.5	38.5	64.5	86.0	94.8	99.1	99.8	
1.3	100	0.	2.5	10.0	30.0	48.8	73.7	90.6	96.9	99.7	100.0	
1.5	100	0.	4.7	16.4	37.5	59.4	79.7	92.6	97.6	100.0		
1.7	100	1.0	8.57	21.9	43.3	66.6	84.8	94.3	99.0			
1.9	100	1.8	12.1	27.8	50.9	73.7	88.6	95.9	100.0			
2.1	100	3.0	16.1	32.7	55.0	78.2	91.0	97.3				
2.3	100	4.2	20.1	36.8	60.7	81.5	92.7	98.8				
2.5	100	5.7	22.8	41.1	64.3	84.8	93.9	99.2				
2.7	100	8.1	25.7	46.0	68.5	85.5	95.5	100.0				
2.9	100	10.1	28.2	49.5	72.3	88.3	96.8					
3.1	100	11.9	31.9	53.8	75.6	90.7	97.5					
3.3	100	13.9	34.3	57.6	78.8	92.7	98.6					
3.5	100	15.7	37.4	61.7	81.7	94.8	99.6					
3.7	100	17.7	40.6	64.6	84.4	96.9	100.0					
3.9	100	18.8	43.7	68.8	87.5	97.5						
4.1	100	20.6	47.1	72.1	89.7	98.6						
4.3	100	22.0	49.2	76.3	91.5	100.0						
4.5	100	24.0	52.0	80.0	94.0							
4.7	100	26.2	54.8	83.4	95.3							
4.9	100	28.6	57.2	85.7	97.2							
5.1	100	31.0	58.6	89.7	100.0							
5.3	100	37.5	62.5	91.7								
5.5	100	45.0	65.0	100.0								
5.7	100	50.0	68.8									
5.9	100	61.5	77.0									
6.1	100	70.0	90.0									
6.3	100	75.0	100.0									
6.5	100	85.7										
6.7	100	92.5										
6.9	100	100.0										
7.1	100											
t in sec. =	0.5	1.	2.	4.	8.	16.	32.	64.	128.	256.	512.	
$n \times 10^{12} =$	0.074	0.148	0.295	0.59	1.18	2.35	4.7	9.4	18.8	37.6	75.2	
E in erg =	0.338	0.675	1.25	2.49	4.98	9.95	19.9	39.8	79.5	159.	318.	

* $\lambda = 460 \mu\mu$.

lowest exposures, but it cannot be stated at present if this is real or apparent.

2. *Densitometry*.—Another series was run using the same

TABLE XVI.
Graflex CrO₃ Treated. Percentage Grains Developed.

Class Size.	Orig. Emul.	Steps 1 to 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10	Step 11
0.11	100	Too erratic to determine.	0.	0.	0.	0.	5.1	13.3	19.7
0.3	100		0.	0.	0.	1.1	10.0	29.2	40.1
0.5	100		0.	0.	0.	6.6	19.8	42.1	57.9
0.7	100		0.	2.2	8.4	17.8	33.8	57.1	73.3
0.9	100		4.7	11.7	20.7	33.3	47.3	72.7	85.3
1.1	100		13.1	20.6	29.9	42.0	61.7	82.7	92.4
1.3	100		18.8	26.9	36.9	50.0	69.4	88.1	96.0
1.5	100		23.4	32.8	42.2	56.6	76.2	92.2	97.2
1.7	100		26.7	36.4	46.7	63.8	80.4	93.3	98.5
1.9	100		29.2	39.3	50.9	68.0	84.2	95.4	99.3
2.1	100		31.3	41.4	55.0	72.0	87.4	96.5	100.0
2.3	100		33.2	44.4	58.2	75.7	90.4	97.5	
2.5	100		34.2	46.8	61.2	78.7	92.0	98.5	
2.7	100		35.6	49.5	63.5	81.6	94.2	99.5	
2.9	100		36.7	52.1	67.6	84.6	96.3	100.0	
3.1	100		38.1	54.4	70.0	87.5	97.5		
3.3	100		39.4	56.9	73.0	89.8	98.6		
3.5	100		40.9	59.1	75.6	92.2	100.0		
3.7	100		41.7	61.5	79.2	93.8			
3.9	100		42.5	62.5	81.2	96.2			
4.1	100		44.1	64.7	83.8	98.5			
4.3	100		45.8	66.1	86.4	100.0			
4.5	100		47.0	68.0	88.0				
4.7	100		48.8	70.2	90.5				
4.9	100		50.6	72.0	92.9				
5.1	100		52.4	74.8	94.8				
5.3	100		54.2	77.0	96.7				
5.5	100		55.0	80.0	99.0				
5.7	100		56.3	81.9	100.0				
5.9	100		57.7	84.6					
6.1	100		60.0	87.0					
6.3	100		61.3	88.7					
6.5	100		62.9	91.4					
6.7	100		65.0	93.3					
6.9	100								
7.1	100								
t in sec. =			32.	64.	128.	256.	512.	1024.	2048.
$n \times 10^{12} =$			4.7	9.4	18.8	37.6	75.2	150.4	300.8
E in erg.			19.9	39.8	79.5	159.	318.	636.	1272.

treatment, but instead of removing the silver the undeveloped silver halide was fixed out and the "densities" measured with a thalofide cell.⁵⁴

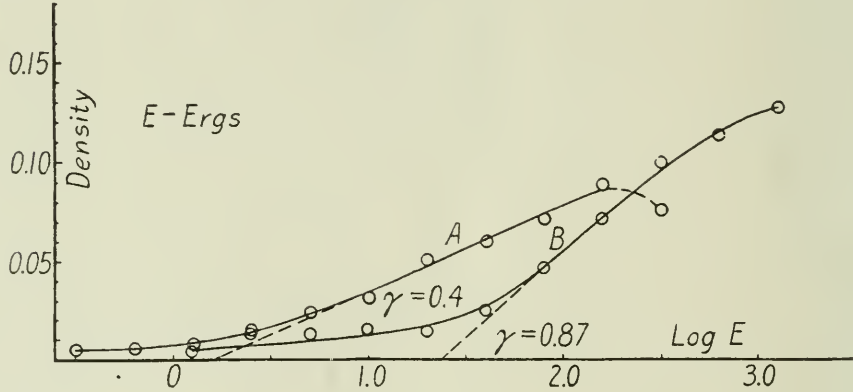
⁵⁴ By Mr. A. L. Schoen of the Physics Department. The instrument is described in the *J. Am. Opt. Soc.*, 7, 483 (1923).

TABLE XVII.
Graflex Ratio. Untreated to Treated.

Class Size.	Steps 5/3	Steps 6/4	Steps 7/5	Steps 8/6	Steps 9/7	Steps 10/8	Steps 11/9
0.11				∞	(2.31)	2.33	2.15
0.3				4.54	2.72	(1.78)	1.70
0.5			∞	3.42	2.57	1.78	1.47
0.7		1.82	2.06	1.95	2.02	1.49	1.26
0.9	0.28	1.11	(1.35)	(1.52)	1.66	1.27	1.13
1.1	0.43	1.04	(1.29)	1.54	1.39	1.15	1.07
1.3	0.53	1.11	(1.32)	1.47	1.30	1.10	1.04
1.5	0.70	1.14	1.41	1.41	1.22	1.06	1.03
1.7	0.82	1.19	1.43	1.33	1.17	1.06	1.02
1.9	0.95	1.29	1.45	1.30	1.30	1.14	1.01
2.1	1.04	1.33	1.42	1.26	1.11	1.04	1.00
2.3	1.11	1.37	1.40	1.22	1.09	1.03	
2.5	1.20	1.37	1.39	1.19	1.08	1.01	
2.7	1.29	1.38	1.36	1.17	1.06		
2.9	1.35	1.39	1.31	1.14	1.04		
3.1	1.41	1.39	1.30	1.11	1.03		
3.3	1.46	1.38	1.27	1.10			
3.5	1.51	1.38	1.25	1.08			
3.7	1.55	1.37	1.22	1.07			
3.9	1.62	1.40	1.20	1.04			
4.1	1.63	1.39	1.18				

In Tables XVIII and XIX are given the densities, corresponding exposures, and exposure logs, and in Fig. 9 the

FIG. 9.



curves *A* and *B* show the untreated and treated emulsion results, respectively. The increase in the steepness of the curve is explainable on the ground of the reduction of the sensitivity

TABLE XVIII.

Density-Exposure Values, Untreated Graflex Emulsion. One-grain-layer Plate.

<i>E</i> in Ergs.	Log <i>E</i>	<i>D</i> ₁	<i>D</i> ₂	<i>D</i> ₃	<i>D</i> ₄	<i>D</i> ₅	<i>D</i> ₆	<i>D_m</i>	Step No.
0.31	1.491	.0043	.0000	.0048	.0086	.0000	.0034	.0042	1
0.62	1.792	.0086	.0022	.0065	.0030	.0048	.0000	.0050	2
1.24	0.093	.0191	.0022	.0111	.0000	.0073	.0000	.0066	3
2.48	0.395	.0294	.0060	.0228	.0170	.0048	.0034	.0139	4
4.97	0.696	.037	.0120	.0588	.0199	.0133	.0145	.0237	5
9.94	0.997	.0386	.0170	.0611	.0199	.0228	.0289	.0314	6
19.88	1.299	.0607	.0358	.0906	.0314	.0434	.0461	.0513	7
39.75	1.599	.0618	.0473	.0806	.0445	.0445	.0817	.0601	8
79.5	1.900	.0849	.0418	.0806	.0596	.0697	.0941	.0713	9
159.0	2.201	.0871	.0565	.1052	.0853	.0697	.1222	.0877	10
318.0	2.502	.0607	.0810	.0871	.0781	.0759	.0685	.0752	11

TABLE XIX.

Density-Exposure Values, CrO₃ Treated Graflex Emulsion. One-grain-layer Plate.

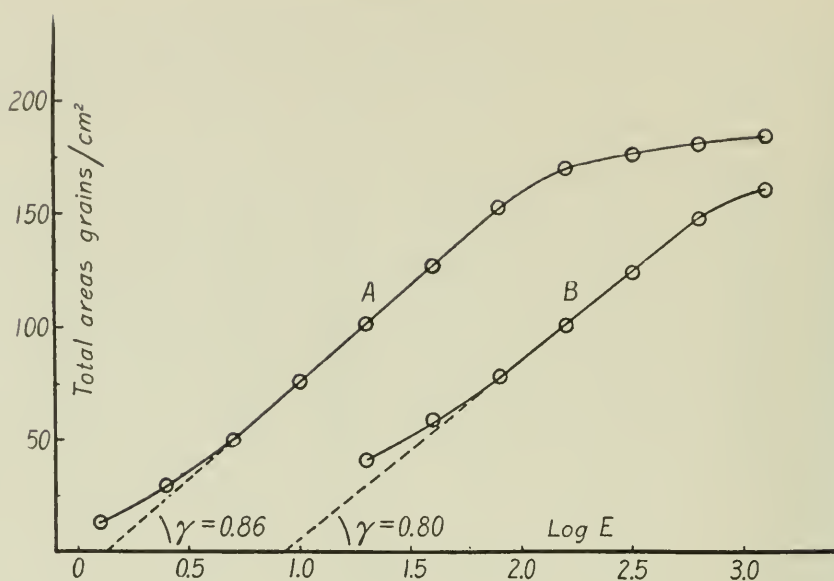
<i>E</i> in Ergs.	Log <i>E</i>	<i>D</i> ₁	<i>D</i> ₂	<i>D</i> ₃	<i>D</i> ₄	<i>D</i> ₅	<i>D</i> ₆	<i>D_m</i>	Step No.
1.24	0.093	.0021	.0178	.0038	.0000	.0021	.0000	.0043	1
2.48	0.395	.0115	.0244	.0119	.0086	.0115	.0086	.0128	2
4.97	0.696	.0178	.0293	.0000	.0115	.0115	.0056	.0126	3
9.94	0.997	.0115	.0350	.0000	.0145	.0257	.0021	.0148	4
19.88	1.299	.0051	.0350	.0060	.0195	.0145	.0056	.0142	5
39.75	1.599	.0051	.0386	.0149	.0350	.0386	.0145	.0245	6
79.5	1.900	.0178	.0685	.0488	.0599	.0461	.0386	.0466	7
159.0	2.201	.0350	.0809	.0755	.0969	.0726	.0659	.0711	8
318.0	2.502	.0468	.1172	.0889	.1212	.1105	.1078	.0987	9
636.0	2.804	.0625	.1616	.1112	.1142	.1215	.1078	.1131	10
1272.	3.104	.1075	.1798	.1112	.1649	.1076	.0909	.1270	11

range by chromic acid treatment.⁵⁵ There is, however, a discrepancy if instead of *density* the total area of developed grains is plotted in both cases (Fig. 10). Here the curves are *parallel*, only the "speed" being altered, *i.e.*, the intercept on the log *E* axis. The reasons for this disagreement are not yet clear;

⁵⁵ Cf. paper sent to Faraday Society Symposium, May, 1923, also G. I. Higson and F. C. Toy, *Phot. J.*, 63, 68 (1923).

Similar results were obtained by using an acid permanganate solution in place of the chromic acid. The concentration of KMnO₄ required to give approximately equivalent results, however, was much lower (about 1/3) than that of the CrO₃.

FIG. 10.



they may be connected with the uncertainty in the correct relation of density = $\log \frac{I}{T}$ with mass of material for one-grain layers, or in the method of determining density by means of the thalofide cell densitometer.⁵⁶ Figs. 11a and 11b and 12a and 12b show photomicrographs of the untreated and CrO_3 -treated grains in alternate exposure steps, (a) with developed silver and (b) the same places after removal of the silver. The arrows indicate where clumping has taken place in the lower and medium exposures.

3. *Action of Chromic Acid and Iodide on One-grain Layers.*—In Table XX are given the effects on the developable threshold values.

The values given in this table are only rough approximations. In the above work the same developer (Fe'' oxalate) was used throughout. Further work is planned making use of a special iodide developer as suggested by Renwick.⁵⁷

As shown by Renwick⁵⁸ and corroborated by our own experiments, treatment with iodide at 1 per cent. concentration shatters

⁵⁶ Cf. P. G. Nutting, *Phil. Mag.*, **26**, 423 (1913); also L. Silberstein, *ibid.*, **45**, 1069 (1923).

⁵⁷ F. F. Renwick, *J. Soc. Chem. Ind.*, **39**, 156T (1920).

⁵⁸ F. F. Renwick, *loc. cit.*

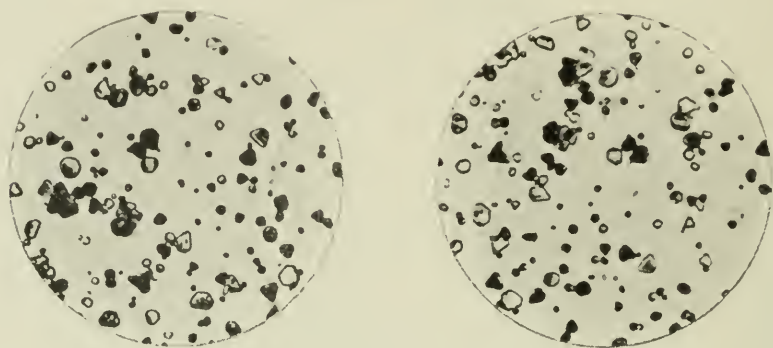
TABLE XX.
Relative Sensitivity, Based on Developable Threshold Value of CrO₃ and KI Treated One-layer Plates.

	I	2	3	4	5
	Blank; exposed without treatment.	0.5% CrO ₃ + 0.2% H ₂ SO ₄ ; washed in 1% NaHCO ₃ ; then in 1% HCl; then in H ₂ O; dried; exposed and developed.	0.5% KI for 15 min.; washed in H ₂ O; dried; exposed and developed.	CrO ₃ treatment as in (2) followed by KI as in (3); washed, dried, etc.	CrO ₃ as in (2); KI as in (3); CrO ₃ again as in (2); washed, dried, etc.
Relative exposure of step I, for each treatment.	I	4	16	16	16
First visible step No.	2	5	7	7	11
Corresponding relative exposure of first visible step.	I	32	512	512	16,384 if at all.

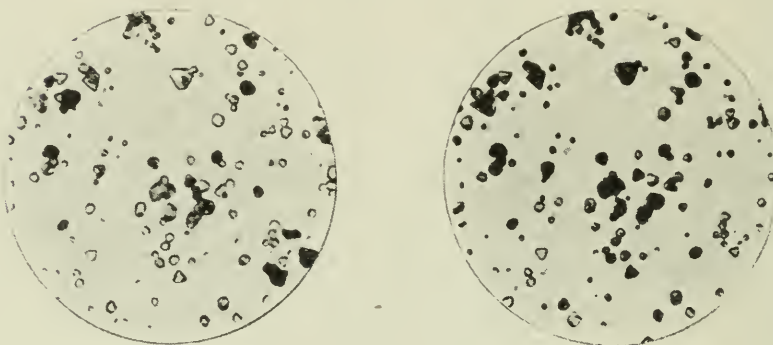
the silver halide grain into a mosaic of finer particles. Developability by ordinary developers is lowered considerably more than by chromic acid.

Since AgI is much less soluble than AgBr, it is probable that

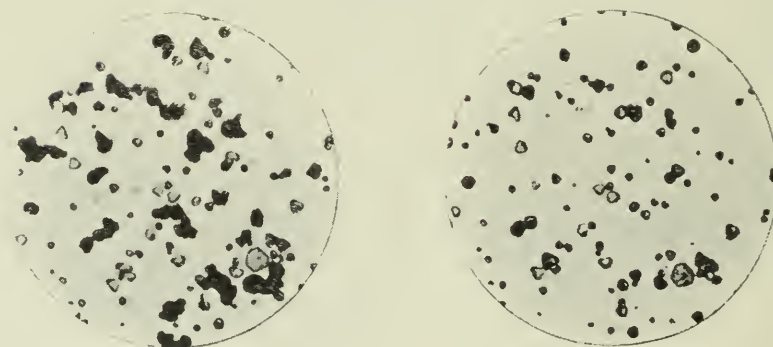
FIG. 11a.



Step 1.



Step 3.



Step 5.

Before Ag removed.

After Ag removed.

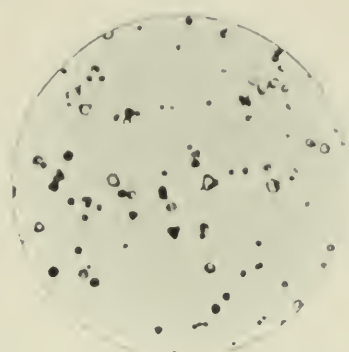
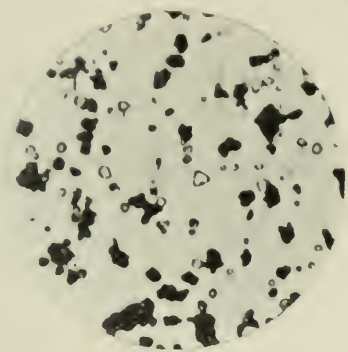
Seed Graflex untreated, exposed and developed.

this effect is primarily a question of reducing the silver-ion solution tension. The fact that AgI, as shown by Lüppo-Cramér and by Renwick, is relatively more easily developed, and gives

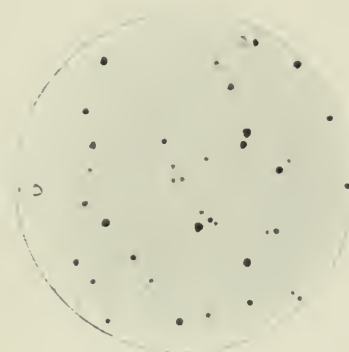
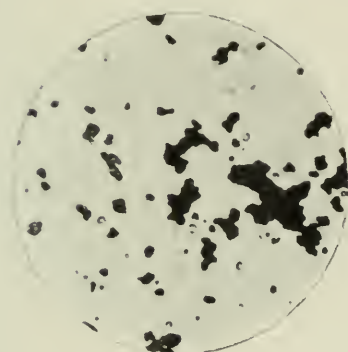
higher sensitivity than AgBr, with physical developers, which supply free Ag^+ ions, supports this view.

The existence of internal sensitive nuclei or spots in the grain prior to exposure seems to be substantiated by the following

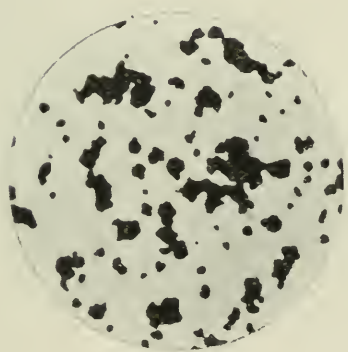
FIG. 11b.



Step 7.



Step 9.



Step 11.

With Ag.

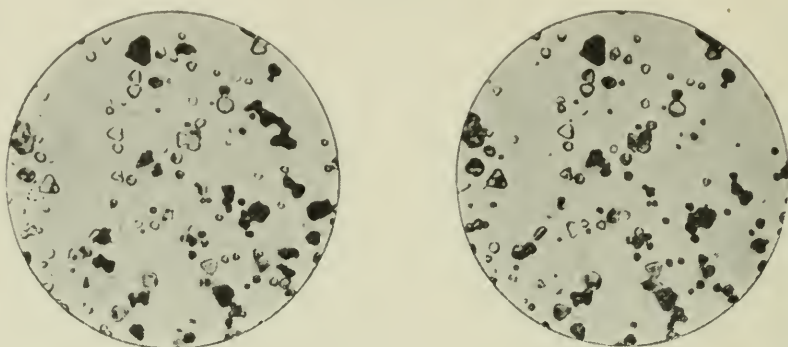
Without Ag.

Untreated, exposed, etc.

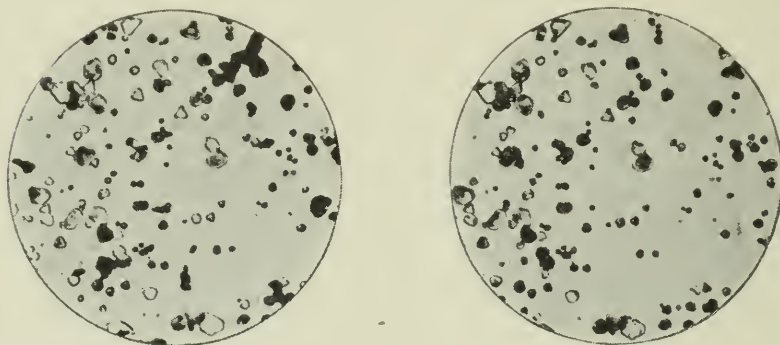
results: Consider two sets of AgBr grains, one from which the surface nuclei have been largely removed by chromic acid, the other not. On treating both with 1 per cent. KI we should expect

the grain stripped of surface nuclei to show still less "sensitivity" than the untreated one; actually they are both of the same (lowered) sensitivity with chemical development. Microscopic examination of the developed grains treated with CrO_3 followed

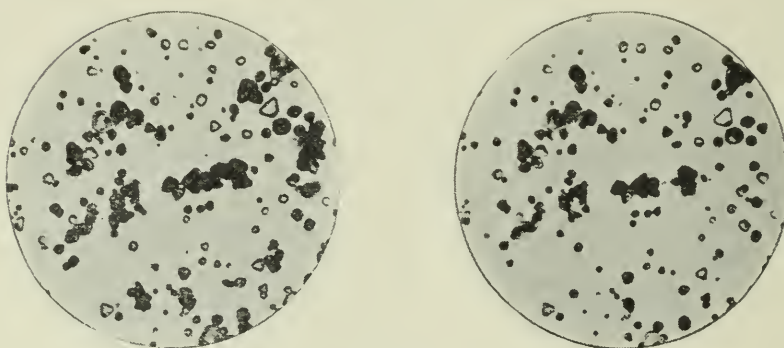
FIG. 12a.



Step 1.



Step 3.



Step 5.

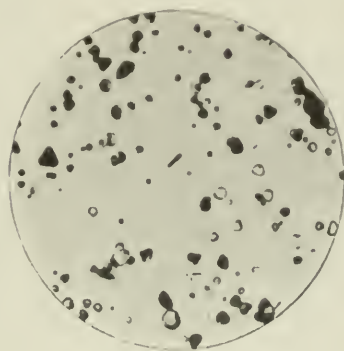
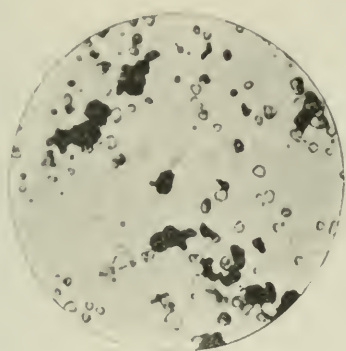
With Ag.

Without Ag.

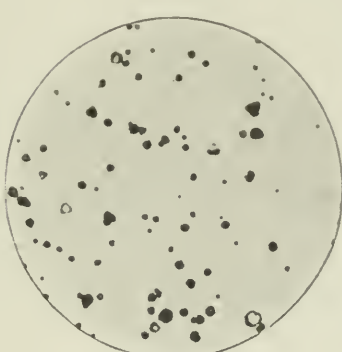
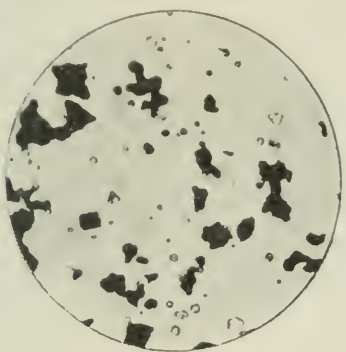
Seed Graflex, CrO_3 treated.

by KI shows that they develop from the centre outward. This also tends to support the view that occluded internal nuclei are freed by the iodide, although it may be due to persistence of

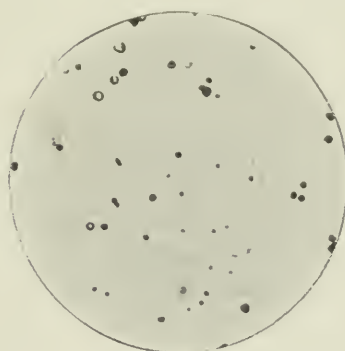
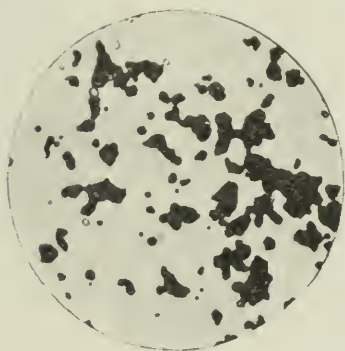
some AgBr. Much more conclusive evidence of the freeing of internal sensitivity nuclei is the fact that further treatment, after the KI, by CrO_3 , again enormously reduces the sensitivity (at least 16,000 times the original sensitivity).

FIG. 12*b*.

Step 7.



Step 9.



Step 11.

With Ag.

Without Ag.

 CrO_3 treated.

The results with CrO_3 alone indicate that the "sensitivity nuclei" are only incompletely removed by CrO_3 —actual figures with sensitometric control on different plates will be given in a

later paper. The subsequent action of KI and CrO_3 indicates that much of the sensitivity is occluded, and may be released by certain means. The action of iodide here is in good agreement with the part played by the "latent image," and points to a similar nature of the "latent image" and "sensitivity," *viz.*, colloid silver. We regard this work as substantiating Lüppo-Cramer's "Keimblosslegung" theory so far as relatively strong iodide solutions are concerned, but consider that with the very dilute solutions adsorption effects are more important.

The work reported has been extended over a considerable time, and our thanks are due to several helpers in the experimental and statistical work and particularly W. H. Davis, R. F. Quirk, A. M. Burgess, and Miss B. M. LeBar.

America's Supremacy over Germany in the Dye Industry.—Professor J. H. James, head of the Department of Chemical Engineering, at the Carnegie Institute of Technology, in Pittsburgh, says that such supremacy "is evidenced by the fact that the United States now produces about 93.5 per cent. of the dyes actually consumed in the country. While it is still necessary for us to import the other 6.5 per cent. from Germany and Switzerland, and which percentage represents only the latest developments of dye manufacture in these two countries, it is clear that America's ability to shift for itself in the dye industry is an indication that, eventually, it will supply most of the dyes to the world."

In tracing the scientific development of the dye industry in this country, and the remarkable progress it has made since 1914 when the war shut off the supply coming from Germany, forcing America to shift for itself for its dyes, Professor James said: "Germany was the home of the dye industry and had done more scientific research along these lines than any other country on the face of the globe up to the time of the war. From 1870 to 1914, which is commonly referred to by students of industrial chemistry as the 'golden age' of German dye-stuff manufacture, there took place the most wonderful development in chemical manufacture in the history of the world. It was during that period that the German government extended long-term credits to the firms interested in research work and development of this kind, and the manufacture of this product. And it was during that time that Germany made itself known everywhere as the leading dye country of the world."

H. L.

PRESENTATION OF THE FRANKLIN MEDAL AND
CERTIFICATE OF HONORARY MEMBERSHIP,
MAY 16, 1923.

At the Stated Meeting of the Committee on Science and the Arts, held January 3, 1923, the following resolutions were adopted:

"*Resolved*, That The Franklin Medal be awarded to General G. Ferrié in recognition of his long-continued and successful researches in the field of radio-transmission of intelligence and their splendid and successful military applications, and of his eminent success in the organization and directing of the communication service of the French Army during the World War."

"*Resolved*, That The Franklin Medal be awarded to Dr. Albert A. Michelson in recognition of his numerous and signally fruitful researches in physical science, especially his brilliant discoveries in the fields of optics and astrophysics."

CORRESPONDENCE.

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia

OFFICE OF THE SECRETARY

FEBRUARY 2, 1923.

General G. Ferrié,
*Inspecteur des Services de la Télégraphie
Militaire et des Transmissions,
51 bis, Boulevard Latour-Maubourg,
Paris, France.*

SIR:

I have the honour to inform you that The Franklin Institute has awarded you The Franklin Medal, founded for "the recognition of those workers in physical science and technology, without regard to country, whose efforts in the opinion of the Institute have done most to advance a knowledge of physical science or its applications." The award is minuted as follows:

"That The Franklin Medal be awarded to General G. Ferrié in recognition of his long-continued and successful researches in the field of radiotransmission of intelligence and their splendid and successful military applications, and of his eminent success in the organization and directing of the communication service of the French Army during the World War."

The medal and accompanying certificate are being prepared, and His Excellency M. Jusserand, your Government's Ambassador at Washington is

being requested to come to the Institute on the afternoon of Wednesday, May 16th, to receive from our President, Dr. Walton Clark, this medal and certificate on behalf of his Government for you.

I am,

Respectfully,

(Signed) R. B. OWENS,
Secretary.

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia

OFFICE OF THE SECRETARY

FEBRUARY 2, 1923.

*His Excellency M. J. J. Jusserand,
Ambassador Extraordinary and Plenipotentiary,
Republic of France, French Embassy,
Washington, D. C.*

YOUR EXCELLENCY :

I have the honour to inform you that The Franklin Medal has again been awarded to one of your distinguished countrymen, General G. Ferrié, Inspecteur des Services de la Télégraphie Militaire et des Transmissions, 51 bis, Boulevard Latour-Maubourg, Paris, France. The award is minuted as follows :

“ That The Franklin Medal be awarded to General G. Ferrié in recognition of his long-continued and successful researches in the field of radiotransmission of intelligence and their splendid and successful military applications, and of his eminent success in the organization and directing of the communication service of the French Army during the World War.”

The medal and accompanying certificate are being prepared and I am requested on behalf of our Management to extend to you a cordial invitation to come to the Institute on the afternoon of Wednesday, May 16th, to receive this medal and certificate from our President for transmission to General Ferrié.

Two Franklin Medals have been awarded this year, one to General Ferrié and one to Dr. A. A. Michelson, Professor of Physics, The University of Chicago.

Our President, Dr. Walton Clark, will shortly extend to you and to Doctor Michelson an invitation to be the guests of honour at a dinner he will give following the presentation ceremonies.

I am

Your Excellency's very humble servant,
(Signed) R. B. OWENS,
Secretary.

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia

OFFICE OF THE SECRETARY

FEBRUARY 2, 1923.

*Dr. A. A. Michelson,
Professor of Physics,
The University of Chicago,
Chicago, Illinois.*

SIR:

I have the honour to inform you that The Franklin Institute has awarded you The Franklin Medal, founded for "the recognition of those workers in physical science and technology, without regard to country, whose efforts in the opinion of the Institute have done most to advance a knowledge of physical science or its applications." The award is minuted as follows:

"That The Franklin Medal be awarded to Dr. A. A. Michelson in recognition of his numerous and signally fruitful researches in physical science, especially his brilliant discoveries in the fields of optics and astrophysics."

The medal and accompanying certificate are being prepared and I am requested, on behalf of our management, to extend to you a cordial invitation to come to the Institute on the afternoon of Wednesday, May 16th, to receive this medal and certificate from our President, Dr. Walton Clark.

I am,

Respectfully,

(Signed) R. B. OWENS,
Secretary.

AMBASSADE
DE LA REPUBLIQUE FRANCAISE
AUX ETATS-UNIS

WASHINGTON, LE FEBRUARY 3, 1923.

DEAR SIR:

My country is sure to deeply appreciate The Franklin Institute's decision to award once more The Franklin Medal to a compatriot of ours, namely, General Ferrié, whose great services in the line of wireless communications will thus be recognized.

It is not possible for me, as you will certainly understand, to be sure in advance that I shall be free on the 16th of May and able to avail myself of the kind invitation of your Institute. If I were prevented to go, I would ask the permission to, at least, be represented on that occasion.

Believe me, with much gratitude,

Sincerely yours,

(Signed) JUSSEMAND.

MR. R. B. OWENS,
*Secretary, The Franklin Institute,
Philadelphia, Pa.*

THE UNIVERSITY OF CHICAGO
RYERSON PHYSICAL LABORATORY

FEBRUARY 7, 1923.

MR. R. B. OWENS,
Secretary, Franklin Institute.

DEAR MR. OWENS:

I have the honor to acknowledge the receipt of your letter announcing the award of The Franklin Medal, and wish to express my gratification and high appreciation of the honor.

I am very strenuously occupied with preliminary experiments preparatory to work at Mt. Wilson, and it may be difficult for me to spare the time for accepting your kind invitation to be present at the meeting of the Institute—especially as I am obliged to attend the Meeting of the National Academy in April.

Very sincerely yours,

(Signed) A. A. MICHELSON.

MINISTÈRE DE LA GUERRE
GÉNIEPARIS LE 24 FEVRIER, 1923,
51 bis, Boulevard Latour-Maubourg (7. arr.)LE GÉNÉRAL FERRIÉ
INSPECTEUR DES SERVICES DE LA TÉLÉGRAPHIE MILITAIRE ET
DES TRANSMISSIONSÀ MONSIEUR R. B. OWENS,
*Secrétaire de l'Institut Franklin,
Philadelphia.*

CHER MONSIEUR:

Je viens de trouver, à mon retour d'une longue absence, la lettre par laquelle vous m'annoncez que l'Institut Franklin m'a décerné la "Médaille Franklin," et je me hâte de vous dire toute ma gratitude pour le grand honneur que m'a été fait. Les termes de la décision de l'Institut, que vous avez bien voulu me communiquer, me touchent d'autant plus qu'ils visent notamment les Services que j'ai pu rendre pendant la guerre mondiale, alors que les Armées de nos deux Pays combattaient côté à côté pour le Droit et la Civilisation, et que leurs "Signal Corps" mettaient en commun toutes leurs ressources, avec la cordialité et l'union les plus complètes. Les sentiments qui sont nés dans de telles conditions ont dans nos cœurs des racines tellement profondes qu'ils ne pourront plus en être détachés.

Je m'efforce maintenant d'étendre aux besoins du temps de paix et au développement de la science les travaux réalisés ou commencés pour notre défense. Les occupations qui m'incombent ne me permettront pas d'aller moi-même recevoir le 16 Mai la Médaille FRANKLIN. Je m'en excuse et je le regrette très vivement.

Veuillez agréer, cher Monsieur, l'expression de mes meilleurs sentiments.
(Signed) FERRIÉ.

AMBASSADE
DE LA REPUBLIQUE FRANCAISE
AUX ETATS-UNIS

WASHINGTON, LE APRIL 25, 1923.

DEAR MR. OWENS:

Referring to previous correspondence and in the last instance to your letter of February the 6th, concerning The Franklin Medal awarded to General Ferrié, I want first to say that I hope you are now quite well and have entirely recovered from the attack of pneumonia from which you suffered this winter.

Concerning the intended ceremony at Philadelphia in the afternoon of the 16th of May, I have to say, to my regret that obligations which I have to fulfill in New York at the same time and which I cannot possibly waive, will prevent my being present. But I hope that you will allow me to be represented and in the thought that this would be agreeable to you, I have designated for this Colonel Dumont, Military Attaché to this Embassy and a veteran of the Great War; he will certainly be a worthy recipient of the Medal destined for one of his brother officers.

Any communication sent to him care of this Embassy would be sure to reach him.

Believe me, with best regards,

Very sincerely yours,

(Signed) JUSSEMAND.

MR. R. B. OWENS,
Secretary of The Franklin Institute,
Philadelphia,
Pa.

AMBASSADE
DE LA REPUBLIQUE FRANCAISE
AUX ETATS-UNIS

WASHINGTON, LE MAY 5, 1923.

DEAR MR. SECRETARY:

I have received this morning the kind invitation of the Officers and Members of The Franklin Institute for Wednesday, May the 16th, at three thirty.

As I wrote to you before, obligations which I must needs fulfill will prevent my being present and having the honor of receiving The Franklin Medal on behalf of General Ferrié, but Colonel Dumont, Military Attaché to this Embassy, will act in my stead.

Believe me, with best regards,

Sincerely yours,

(Signed) JUSSEMAND.

MR. R. B. OWENS,
Secretary of The Franklin Institute,
Philadelphia,
Pa.

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia

MAY 7, 1923.

YOUR EXCELLENCY:

Please accept my best thanks for your kind letter of May 5th.

That you cannot be here on the afternoon of Wednesday, May 16th, is, of course, a matter of regret. If I take no liberty in saying so, I can easily imagine how well every moment of your time is occupied in the highest kind of constructive work, that of bettering an understanding of present day world conditions and maintaining essential international relationships.

Perhaps the Institute's recognition of General Ferrié's splendid work and that of Professor Fabry will have a reflex, however small, in strengthening, if it is possible, those bonds, which, as an Officer in the American Expeditionary Forces, I saw being reforged and welded to a thing of greater strength than I believe the world has ever known before in its history.

The Institute is honoured in having you represented by Colonel Dumont, with whom I have communicated.

Believe me, with kindest regards,

Always sincerely,

(Signed) R. B. OWENS,
Secretary.

*His Excellency, M. Jusserand,
Ambassador, Republic of France,
French Embassy,
Washington, D. C.*

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia

MAY 10, 1923.

DEAR COLONEL DUMONT:

An illness has deprived me of the pleasure of before directly communicating with you relative to the visit, I understand through His Excellency, M. Jusserand, it will be agreeable to you to make us on Wednesday, next.

Referring to the enclosed programme, you will note that General J. J. Carty will make a statement relative to the work of General G. Ferrié, and I may say that General Carty will after making such a statement present you to our President to receive for transmission to General Ferrié the Institute's Franklin Medal, accompanying Certificate and Certificate of Honorary Membership.

I also enclose with this an account of last year's May Meeting, which will give you an idea of the very simple procedure which will be followed next Wednesday. If, after receiving for General Ferrié the medal, etc., you should

make a few remarks, all of us here will be greatly pleased. You will not object, I trust, if I say that the Institute's action in awarding The Franklin Medal to General Ferrié gives me personally a very peculiar and very sincere satisfaction. It was my great privilege as a Signal Corps Officer, A.E.F., to know General Ferrié and to be the recipient of many kindnesses extended by him. For him as a scientist, an engineer, and a soldier, I have an intense admiration and for him as a man I have great affection, and I can assure you that my feelings toward him are shared by every American Officer who had the privilege of knowing him.

I am also enclosing a paper "The Scientific Applications of Radiotelegraphy" by General Ferrié, which will be read by our mutual friend, General G. O. Squier, Chief Signal Officer, U. S. Army.

My thought is that it will perhaps be convenient to you and to General Squier to take the Pennsylvania R. R. train leaving Washington at 8.15 A.M., arriving West Philadelphia 11.24, and to have luncheon with me and with Dr. A. A. Michelson at the Philadelphia Club, 1301 Walnut Street, about one o'clock (daylight saving).

I have taken the liberty of asking a few gentlemen to meet you and Doctor Michelson at dinner on Wednesday evening.

Believe me, with kindest regards,

Always sincerely,

(Signed) R. B. OWENS,
Secretary.

*Colonel G. A. L. Dumont,
Military Attaché, French Embassy,
Washington, D. C.*

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia

OFFICE OF THE PRESIDENT

MARCH 21, 1923.

DEAR DR. MICHELSON:

I have been very sorry to learn that there is some doubt of your ability to be present at The Franklin Institute on May 16th to receive The Franklin Medal, awarded to you in recognition of your wonderful services to mankind rendered in the field of physical science. I hope very much that you will be able to arrange to be with us to receive the medal in person.

With kind regards,

Respectfully,

(Signed) WALTON CLARK,
President.

*Dr. A. A. Michelson,
Professor of Physics,
The University of Chicago,
Chicago, Illinois.*

THE UNIVERSITY OF CHICAGO
RYERSON PHYSICAL LABORATORY

MARCH 30, 1923.

MR. WALTON CLARK, M.E., D.Sc.,
President, Franklin Institute.

DEAR DR. CLARK:

I greatly appreciate your letter of the 21st instant. It will be difficult for me to adjust certain engagements to which I am committed, but I am nevertheless glad to accept your kind invitation to be present on May 16 next to receive The Franklin Medal from you.

Very sincerely yours,

(Signed) A. A. MICHELSON.

STATED MEETING
WEDNESDAY, MAY 16, 1923
3.30 O'CLOCK

PROGRAMME

PRESENTATION OF

THE FRANKLIN MEDAL
ACCOMPANYING CERTIFICATE AND CERTIFICATE OF
HONORARY MEMBERSHIP

TO

COLONEL G. A. L. DUMONT
MILITARY ATTACHÉ, THE FRENCH EMBASSY

REPRESENTING

HIS EXCELLENCY M. JUSSERAND
AMBASSADOR EXTRAORDINARY AND PLENIPOTENTIARY
THE FRENCH REPUBLIC

FOR

GENERAL G. FERRIÉ
INSPECTOR GENERAL OF MILITARY COMMUNICATIONS
THE FRENCH ARMY

PRESENTATION OF

THE FRANKLIN MEDAL
ACCOMPANYING CERTIFICATE AND CERTIFICATE OF
HONORARY MEMBERSHIP

TO

ALBERT A. MICHELSON

PAPERS

THE SCIENTIFIC APPLICATIONS OF RADIOTELEGRAPHY

GENERAL G. FERRIÉ

READ BY MAJOR GENERAL GEORGE OWEN SQUIER
CHIEF SIGNAL OFFICER, U. S. ARMY

LIGHT WAVES IN ASTRONOMY

ALBERT A. MICHELSON

THE PRESENTATION OF THE FRANKLIN MEDAL AND
CERTIFICATE OF HONORARY MEMBERSHIP TO
GENERAL G. FERRIÉ AND DR. A. A.
MICHELSON.

IN calling the meeting to order the President of the Institute announced that the business of the meeting would be the annual presentation of the Institute's highest award, The Franklin Medal, in recognition of distinguished scientific and technical achievements and recognized Brigadier-General John J. Carty, Vice-president of the American Telephone and Telegraph Company, who made the following statement relative to the work of General G. Ferrié:

The Franklin Medal was founded in the year 1913 through the beneficence and generosity of Samuel Insull, Esq., of Chicago. The medal is to be awarded from time to time in recognition of the total contributions of individuals to science. The award is to be made without regard to country, and to those who have done most to advance the knowledge of physical science or its applications.

To-day the medal is to be awarded to General G. Ferrié, Inspector-General of Military Communications in the French Army. The award is to be made "In recognition of his long-continued and successful researches in the field of radio transmission of intelligence and their splendid and successful military application, and of his eminent success in the organization and directing of the communication service of the French Army during the World War."

General Ferrié possesses in a high degree the qualities of soldier, scientist, and engineer. He will be remembered as one of the most distinguished pioneers in the art of radio transmission. Since the year 1898 he has devoted himself to the study of the new science, the wonderful possibilities of which were revealed by the work of Branly and Marconi. Independently of others, he developed the electrolytic detector, and he was the first to apply radiotelegraphy in the French colonies, notably between Martinique and Guadeloupe, where the wireless telegraph system which he designed rendered such important service after the destruction of the cable caused by the eruption of Mt. Pelée.

As early as 1903, he began the study and later the construction of a radiotelegraph station on the Eiffel Tower, the first

of the great French stations. Subsequently in Morocco in 1908, he began the establishment of a wireless telegraphic network for military purposes, made up of stations throughout that area, which assured communications between the different units of the expeditionary forces.

During these years he also developed measuring apparatus, providing valuable methods for use in the transmission of time by radiotelegraph, thus contributing to the progress of navigation and the science of geodesy. It is to General Ferrié that France owes the splendid organization of the radiotelegraph service for the French army, and which in the course of the war rendered results of such incalculable value. After the month of July, 1914, he caused the construction of a new radiotelegraph station at Lyons. This was done with remarkable speed, and rendered service of immense consequence, carrying the extra load of messages which could not be carried by the Eiffel Tower. During the war, he organized powerful groups of scientists and engineer officers and university professors who, working under his direction, produced devices of great military value. It was under his direction that apparatus for the sending and receiving of wireless messages using electric valves was put into effect in the French armies, thus giving to the Allies agencies of communication superior to those of the enemy.

He also developed a method of telegraphing through the ground, and for communicating with dirigibles and airplanes. He introduced improved forms of radiogoniometric apparatus for locating the radio stations of the enemy. He did pioneer work in experiments for directing the course of airships and warplanes operating without pilots.

He is a member of many commissions and technical committees, both national and international, where his scientific ability and large experience of affairs are productive of great good. He was a member of the International Radiotelegraph Conference at London in 1912, the International Congress of Time in 1913, the Interallied Telegraphic Conference of 1920, the Interallied Technical Committee of Wireless Telegraphy, and was technical advisor at the International Communications Conference recently held at Washington.

He has received numerous decorations, both French and foreign, including the Distinguished Service Medals of the United

States Army and of the United States Navy. He is Doctor Honoris Causa of Oxford University, England. The Institute of France awarded him the Kastner Boursault prize in 1904, the Wilde prize in 1912, and the Osiris prize in 1921. Last year he was elected to the Academy of Science of the Institute of France, the highest scientific honour conferred in his country.

In the estimation of the scientists and radio engineers of all the nations, the work of General Ferrié in radio transmission holds a foremost place. His comprehensive knowledge of radio engineering is based upon a sound understanding and thorough grasp of the fundamental scientific principles involved. His remarkable ingenuity and his rare sense of practical values have enabled him to apply to civil affairs the results of pure scientific research, with distinguished success. His professional training as a soldier and his knowledge of military engineering have enabled him to apply his fundamental scientific knowledge to military problems with even greater results. During the period of the colossal conflict of the armies of the world, his modest bearing and the unobtrusive character of his labors served for a time to veil their importance, but now that we are beginning to make an appraisal of that prodigious human effort which won the war, we find that General Ferrié is entitled to high rank among the distinguished generals of France.

In awarding to General Ferrié their Medal, which bears the name of the illustrious philosopher and scientist, Benjamin Franklin, and in electing him to be an Honorary Member of their organization, the members of The Franklin Institute are paying to him the highest tribute which they can offer to a man of science. But this award contains another tribute—a recognition of the long-continued friendship between General Ferrié and his hosts of friends in the American Army and Navy and in civil life. He has coöperated with the United States Navy in time of peace and in time of war, and his numberless services to the American Expeditionary Forces and particularly to the Signal Corps and its scientific staff in France, will always be held in grateful remembrance.

It is fitting that I should at this time speak of that historic event in the annals of electrical communications when in October, 1915, speech was for the first time transmitted by telephone across the Atlantic Ocean. This was achieved as a result of work car-

ried out by that distinguished staff of scientists with whom I have the honour to be associated. The words were spoken into apparatus located at the Arlington radio station of the United States Navy, and they were heard at the Eiffel Tower by members of my staff whom I sent there for that purpose, by a representative of the United States Navy, and by General Ferrié and members of his staff. If it were not for the historic friendship which exists between the United States and France, and if it were not for the sympathetic consideration of General Ferrié towards Americans, and his devotion to science even during the darkest period of the war, this result could not have been achieved. To General Ferrié, therefore, goes the gratitude alike of the American and French scientists, for without his coöperation it could not be said that the first words ever spoken across the Atlantic Ocean passed between the two great Republics, the United States of America and France.

To-day, the Franklin Medal takes on new dignity and importance, for it has become a token of that historic friendship between France and America which was so firmly established by the mission of Benjamin Franklin to France, and which, having been again affirmed and hallowed by the ties of blood, can never be destroyed.

The President then said:

I desire, Colonel Dumont, before proceeding with the presentation of Franklin Medals—which is the business which has brought us together—to say to you and to our other guests that the Management of The Franklin Institute are highly sensible of the distinction added to this occasion by the presence of an official representative of the French Republic.

Sir, I have the honour, in the name of The Franklin Institute, to present to you, for transmission to your distinguished countryman, General G. Ferrié, The Franklin Medal and a Certificate of Honorary Membership in the Institute. This award with honorary membership is made to General Ferrié in recognition of his distinguished services to mankind rendered in the fields of pure and applied science. They are the highest honours in the gift of the Institute.

Colonel Dumont, in accepting the Medal and the Certificate of Honorary Membership said:

Monsieur President and Gentlemen: It would have given His

Excellency Monsieur Jusserand, the French Ambassador, the greatest pleasure to be present here to-day in order to receive, at your hands, in the name of France, The Franklin Medal and the Certificate of Honorary Membership in The Franklin Institute which you have awarded to General G. Ferrié, honours which you bestow only on eminent living scientists.

Unfortunately, the heavy duties of Monsieur Jusserand, heavier still as you may know, at the present time, have prevented him from coming to Philadelphia and he has entrusted me with the commission of acting on his behalf, during this ceremony.

Being neither a diplomat nor a scientist, I imagine that my being occasionally dressed up in the horizon blue uniform of France was one determining reason for my appointment, so that I do take a great deal of pride in representing on this occasion not only my dear old country at large, but in a quite special way the French Army, to which belongs the scientist you have chosen to honour. But at the same time how humble I feel amidst this distinguished company when reminded of what happened some thirty-six or thirty-seven years ago, when having, together with Ferrié, entered the competition in order to be admitted to our Polytechnic School, Ferrié was successful and myself hopelessly left behind the gates.

Now, this did not happen because he knew much more than myself or any one of us, about electricity—in fact, in 1886–1888 our professors had been so upset by these wonderful inventions, the telephone, the phonograph, others of the same kind, many of them, I must say, coming from this country, and displayed in Paris on the occasion of the special exhibition held in the old “Palace of Industry,” that they had decided to suppress entirely for the time being, that part of the programme for admission.

Only ten years after he had been commissioned an officer in the Army, did Ferrié (as recalled by General John J. Carty) really begin to specialize in the work which was to bring him to preëminence, and gain for him the honours of to-day, so that he little thought, I am sure, in those old days I have taken the liberty of recalling, that, some time, he should sit night after night on the watch in this country, at Fort Meyer near Washington, anxiously trying to receive radio signals and messages from Paris.

What more can I say, after the tribute paid by General Carty, and in the presence of our mutual friend and brother in arms, Major General G. O. Squier, Chief Signal Officer of the U. S.

Army. Only this, maybe, because I know it to be true, General Ferrié is so devoted to science that these honours bestowed upon him, he does not consider them as merely the crowning of his past achievements but rather as an encouragement to keep in constant progress his research work, in close touch with his American friends, for the benefit not only of his country but of the entire world, because science having no limitations, ignores land boundaries.

America and France, both under the red, white and blue colors, enjoying the same ideals, the same eagerness for knowledge, the same love for liberty, have been in the past, and are now, so much in the heart of one another, that I hardly need conclude these few remarks in expressing my sentiment that this award is another token, after many others, of that real warm friendship which exists between our countries, our scientific associations, our public and private citizens, a friendship which like radio ignores time and space.

Dr. Arthur L. Day, Director of the Geophysical Laboratory of the Carnegie Institution of Washington, was then recognized and made the following statement concerning the work of Dr. A. A. Michelson:

It is our privilege to-day to bestow upon a distinguished physicist the highest award within the gift of this great Institute. The Franklin Medal, says the founder, shall be awarded "to those workers in physical science or technology . . . whose efforts have, in the judgment of the Institute, done most to advance a knowledge of physical science or its application." There are many other rewards of merit which are given annually by The Franklin Institute, but these commemorate a single preëminent accomplishment. The Franklin Medal alone confers recognition of a career of distinguished achievement in the advancement of our knowledge of physical science and its applications to the welfare of mankind. It is in this distinctive sense that the award of to-day attains to its highest significance, for among living physicists no career has been marked by greater singleness of purpose in the advancement of physical science and none has risen to such heights in the pursuit of that particular ideal of physics, the attainment of exact knowledge, as the one we commemorate to-day.

The most successful worker in the field of physical measurement expects to see results superseded through the development of

superior methods by another, or, as the science advances, to find that a working hypothesis requires revision or extension. In the forty-five years of nearly continuous research activity to which your attention is directed to-day there is hardly a slip or an unnecessary step in the continuous progress to accomplishments never surpassed. The modest note in the *American Journal of Science* for May, 1878, scarcely half a page in length, announcing a new method of measuring the velocity of light in which concave mirrors were dispensed with and the measured light-path might be of any length, is the same method in its essentials as that to be used by the same hand in the redetermination at Mt. Wilson this year. In the first attempt the measured light-path was a few metres, and the accuracy sought approached one part in 10,000, in the last the light-path is more than twenty miles and the accuracy sought, one part in five hundred thousand.

The importance of this constant, both for physics and astronomy, and the prevailing interest in the undulatory theory of light transmission, led to further study of its mechanism and to something very like the modern theory of relativity. The undulatory theory demanded a medium with certain properties (the ether) pervading all space. But the earth moves in space with a considerable velocity. It was therefore necessary to the determination of the absolute velocity of light to know whether the movement of the earth in the ether served to disturb its light transmitting power, and further, whether the velocity was the same when moving in the direction of the earth's motion or contrawise, or at right angles to it. This need for an apparatus to discover differences in the velocity of light along two paths perpendicular to each other gave us the interferometer which has since had a remarkable development and history. It has made it possible to use unchanging wave-lengths of light as our ultimate standards of length, and most small dimensions are now measured by its use.

A few evenings ago at the Carnegie Institution of Washington it was my privilege to listen to Doctor Michelson's own account of his discovery, in the laboratory of Professor Cornu, of the manner of interference of two beams of light meeting in different phase whereby interference bands or fringes are formed, alternately light and dark in monochromatic light, rainbow colored in white light. Professor Cornu was unwilling to accept this interpretation of the fringes without a demonstration and accordingly a primitive interferometer was arranged using white light. Such

a system is not easy to demonstrate satisfactorily under the best of conditions because of the great number of wave-lengths participating in the interference phenomenon and the consequent difficulty of adjustment of the apparatus, and so in the rather nerve-racking atmosphere of a demonstration before a skeptical master it happened that the fringes would not come. I suspect that the sympathy which was freely offered to the embarrassed student was about the last thing in the world which this particular student felt the need of just then, but be that as it may, a later demonstration was successful and brought with it appropriate recognition.

The method has since been employed to measure and compare national standards of length, to measure the rigidity of the earth, to determine the magnitude and the orbits of the satellites of Jupiter, the distance apart of double stars, and recently, in the most spectacular fashion, to determine the diameter of fixed stars where the greatest telescopes, as hitherto used, distinguish only point sources of light. Its accuracy in measurements of length, under favorable conditions, may reach one part in a million, probably surpassing that of any other instrument available to the physicist.

With a directness and a precision equally uncanny the subject of spectroscopy has been developed to a point hitherto undreamed of. The great ten-inch grating with a resolving power of 600,000 and the echelon spectroscope, which surpasses even this accomplishment perhaps seven or eightfold, are masterpieces of technical achievement no less than of ingenious analytical conception.

The determination of the rigidity of the earth and the establishment of a true elastic tidal movement of its solid surface might well stand alone and merit the recognition which The Franklin Institute accords to-day. Such outstanding figures in the physical world as Lord Kelvin and Sir George Darwin were able to wring from this overmastering problem, already several generations old, only so much as to conclude that the earth must have at least the rigidity of steel. With the tiny interferometer and two horizontal tubes 500 feet long and half filled with water Doctor Michelson determined, within less than one per cent., the magnitude, and even more accurately, the period, of the earth's solid tide. The newly recognized science of geophysics records no greater accomplishment than this.

For these services, Mr. President, in the advancement of "a knowledge of physical science" as provided in the deed of gift, I have the honour to present to you Dr. Albert Abraham Michelson, Doctor of Philosophy, of Science and of Laws, Professor of Physics of the University of Chicago, President of the National Academy of Sciences, recipient of the Nobel Prize for Physics (1907) and other awards, member of many learned societies, both American and foreign, to receive The Franklin Medal.

The President, in presenting The Franklin Medal and Certificate of Honorary Membership to Doctor Michelson, said:

I have the honour, in the name of The Franklin Institute, to present to you The Franklin Medal and a Certificate of Honorary Membership in the Institute. This award with honorary membership is made in recognition of your distinguished services to mankind in the field of science. They are the highest honours in the gift of the Institute.

Doctor Michelson, in accepting The Franklin Medal and Certificate of Honorary Membership, said:

Mr. President, Members of the Institute, Ladies and Gentlemen:

General Ferrié has over me the double advantage of being in Paris and of having Colonel Dumont acknowledge the honours that have been showered upon him.

For myself I can only assure you that words fail me, but nothing can exceed my appreciation of the distinguished honour done me. The Franklin Institute has risen in power and glory so that its reputation covers the whole wide world and my hope and faith is that it will so continue to progress, especially through the distinguished efforts of its able President and its efficient Secretary.

I may add that I do not claim any particular merit for the so-called distinguished service I have rendered, I doubt if any scientific man does his work to render distinguished service, I think he does it because it is good fun.

The President then recognized Major General George Owen Squier, Chief Signal Officer, U. S. Army, who read the paper, "The Scientific Applications of Radiotelegraphy," by General G. Ferrié (page 763).

The President then recognized Dr. A. A. Michelson, who read his paper on "Light Waves in Astronomy."

CORRESPONDENCE.

The Editor of the
JOURNAL OF THE FRANKLIN INSTITUTE,
Philadelphia, Pennsylvania.

The letter from Sir William H. Bragg, published in the November issue of your JOURNAL, has just come to my attention. In this letter he takes exception to the pertinence of the emphasis laid upon the theory of space groups in a recent discussion of the results of X-ray crystal analysis [JOUR. FRANK. INST., 195, 183, 349, 531 (1923)]. Your correspondent seems to hold the view that the usefulness of this theory in crystal analysis is limited to the provision of a convenient (or perhaps confusing) "terminology" and that as a consequence the theory can contribute nothing of fundamental value to the study of atomic arrangement. I must dissent from this conclusion.

The essence of the methods which use the results of space group theory is that they aim to give consideration to all of the possible atomic arrangements for a crystal. The ultimate goal is not merely to discover a possible arrangement for the atoms in a crystal which will momentarily satisfy a particular observation, but to ascertain the only arrangement possible, having regard to the basic assumptions which underlie the interpretation of diffraction effects and the deduction of the space group theory. Whether this goal can be reached in any particular instance will depend upon the richness of the available experimental data; but even where it cannot be reached these methods indicate *all* of the other arrangements which remain experimentally indistinguishable and therefore possibly correct. Such knowledge cannot be supplied except by this theory itself or by geometrical considerations equivalent to its content. Both your correspondent and we who use space group theory are agreed in admitting X-ray diffractions as the only acceptable experimental criterion. It is for this reason inevitable that where enough data have been found to establish the structure uniquely (and resorcinol, cited by Professor Bragg, may be such an instance though the published data are inconclusive), the procedures used by him and the methods of crystal analysis using space group results will yield the same atomic arrangement. The point that requires emphasis, however, is this: That only by employing the theory of space groups or equivalent reasoning, can we ever be sure that there may not be a number of other structures in equally good agreement with the limited data then at our disposal.

Viewed in this light the issue resolves itself into a question of the relative scientific merits of two methods; one of these seeks

a possible, the other *the only possible*, solution to a problem. For those who feel that such a formal deduction of unique solutions is unnecessary, reference need only be made to the several cases listed in the previously mentioned discussion appearing in this JOURNAL, in which the older methods have failed to produce correct or necessarily correct crystal structures.

RALPH W. G. WYCKOFF.

Geophysical Laboratory,

Washington, D. C.

November 12, 1923.

Measuring Acceleration by Means of a Flame. K. PRYTZ. (*Jour. Phys. Radium*, June, 1923.)—If a closed lantern containing a burning candle be moved with a constant velocity, the flame retains its customary vertical position. However, upon moving the lantern from right to left horizontally, the axis of the flame at first tilts toward the left during the period of acceleration toward the left, and later, while the velocity is diminishing, it is inclined toward the right. In general the tip of the flame is displaced in the direction of the acceleration. When the lantern is let fall, the tip is displaced downward with respect to the wick and, in fact, the flame is shortened, as is confirmed by experiment.

A discussion of the theory leads to this relation, when the flame has a horizontal acceleration, $a = g \tan \beta$, where a is the acceleration to be measured, g the acceleration of gravity and β is the angle between a vertical line through the wick and the axis of the moving flame. The author suggests that the direction of the flame could be photographed on a film carried along with the lantern. The slight mass of the flame would permit it to follow aperiodically any changes in velocity.

A very interesting proposal for a new kind of dead reckoning is made. Along with the lantern let two automatic, photographic registering devices be mounted on a Cardan suspension in a ship. These should record the direction of the flame axis on two vertical planes at right angles to each other. Thus the direction and amount of the horizontal acceleration at all instants of the voyage could be deduced. Then the hodograph of the voyage could be constructed and from this, in turn, the velocity at each instant. Of course, from a knowledge of the starting-point of the vessel and of its velocities at all times, it is possible to determine its position at any hour. It is true that the pitching of the craft introduces vertical components of acceleration. This error would be reduced by locating the apparatus amidships. Moreover the rapid alternations in direction of these components cause them to have little effect on the final result. "As to knowing whether this method is practical or not, at this time I am unwilling to venture any opinion on this point." G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

A STUDY OF RADIO SIGNAL FADING.¹

By J. H. Dellinger, L. E. Whittemore and S. Kruse.

[ABSTRACT.]

WHEN radio first was used for long-distance communication it was noticed that signals were not transmitted as far during the day as during the night. It has also been observed that the direction from which radio waves are received at a given receiving station varies greatly from time to time, and that short wave signals may vary rapidly in intensity. On account of the dependence of these phenomena upon weather conditions, surroundings of the transmitting and receiving stations, and the nature of the country over which transmission occurs, it is only by a statistical study that reliable conclusions regarding their nature can be obtained.

During the summer and fall of 1920 and the spring of 1921, a series of tests was conducted by the Bureau of Standards in coöperation with the American Radio Relay League. During these tests, signals were transmitted by from five to ten radio stations in succession, test schedules having been arranged in advance for certain specified nights. The signals were received simultaneously by about one hundred receiving stations, whose locations cover the northeastern part of the United States. These tests have confirmed, in a statistical way, what had previously been little more than impressions received by operators and experimenters in the course of receiving radio messages.

Signals from a given transmitting station may be received with violent fading by some receiving stations and simultaneously with very little fading by others. As a result of the statistical analysis of over 5000 records secured during the tests, tables have been prepared giving suggested relationships between the fading and intensity of signals and the prevalence of strays and the weather conditions which existed at the times of transmission. For example, it was observed that general cloudiness over the region between the transmitting and receiving stations has a tendency to produce severe fading.

* Communicated by the Director.

¹ Scientific Papers, No. 476, price ten cents.

As an explanation of the phenomena observed it may be considered that the transmission of radio waves during the daytime is largely along the surface of the earth, that part of the waves which is radiated upward being absorbed by the atmosphere. Night transmission, however, especially for great distances and using short wave-lengths, is probably by means of waves transmitted along the Heaviside surface, a highly conducting layer at a height of about sixty miles above the surface of the earth. Waves at night are thus free from the absorption encountered in the daytime, but are subject to the great variations caused by irregularities of the ionized air at or near the Heaviside surface. The transmission along this surface with relatively little absorption may thus account for the long distances covered at night, while the variations in such absorption as is present probably account for the fading.

DETECTOR FOR WATER VAPOR IN CLOSED PIPES.²

By E. R. Weaver and P. G. Ledig.

[ABSTRACT.]

A SIMPLE device is described for determining the approximate concentration of water vapor in a gas. A glass tube is coated with platinum and the coating divided by etching into two electrodes. Platinum wires, sealed through the glass, connect the electrodes to a measuring circuit. The resistance to alternating current of a thin film of a hygroscopic electrolyte bridging the gap between the electrodes is used as the measure of the water vapor in the atmosphere with which the film is in contact. Sulphuric and phosphoric acids and various hygroscopic salts can be used in forming the conducting film. The detector is simple, rugged, and easily adapted for use in high-pressure piping and other situations in which the determination of water vapor is usually attended with difficulty.

Quantitative determinations with a single detector are possible over only a small range of concentration of water vapor, and must be made under rather carefully controlled conditions. The location of the sensitive range depends upon the hygroscopic substance employed.

Laboratory experiments showing the reliability, method of application and limitations of the device are described.

² Technologic Papers, No. 242, price five cents.

NOTES FROM THE RESEARCH LABORATORY,
EASTMAN KODAK COMPANY.*

QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE, III.¹

By L. Silberstein.

IN this paper account is taken of the absolute energy values (determined experimentally) of the exposure used in the experiments described in the previous papers. It is shown that in the emulsion used not more than one ten-thousandth, and probably not more than about one hundred-thousandth, of the area of a grain is sensitive to light, *i.e.*, made developable on being hit by a single light dart. The probable explanation of this is that only a small minority of all the darts cause developability by ejecting photo-electrons, a result in agreement with photo-electric experiments of Elster and Greitel and Pohl and Pringsheim. Previously it has been assumed that, at any rate for equal-sized grains, the small area of the grain which is especially sensitive is all in a lump, but now the assumption is made that the grain contains a number of separate specially sensitive spots distributed among the individual grains haphazardly, the sufficient condition for grain developability being that at least one of its spots is hit by at least one light dart of a wave-length less than the critical wave-length. It is shown that the main results previously obtained are not altered very much by this assumption. Starting with the elementary equation

$$k = N (1 - e^{-nea})$$

where k = number of grains changed out of the total, N , n = number of quanta incident, a = area of single grain and e = fraction of area a which is specially sensitive, the author deduces the integral or "density" formula for a certain type of emulsion. Comparison with experimental results recently obtained with X-rays shows an excellent agreement, all the differences between the theoretical and observed values being well within the limits of experimental error.

* Communicated by the Director.

¹ Communication No. 173 from the Research Laboratory of the Eastman Kodak Company and published in *Phil. Mag.*, May, 1923, p. 1062.

NOTE ON THE INFLUENCE OF CRYSTAL HABIT ON THE
PHOTOCHEMICAL DECOMPOSITION IN SILVER
BROMIDE CRYSTALS.²

By S. E. Sheppard and A. P. H. Trivelli.

IT is noted that while the visible photochemical decomposition has in common with the initiation of development the property of commencing at isolated points, its further increase may be a relatively orderly process, vectorial in character, and oriented according to definite directions in the crystal. Although the accretion of the photoproduct proceeds mainly by discontinuous increments, the accretion is neither uniform, nor purely haphazard, but radiates along the lines of more rapid growth.

THE CRYSTALLINE STRUCTURE OF SILVER IODIDE.³

By R. B. Wilsey.

IN a preliminary note (*Phil. Mag.*, 42, 262, 1921) the author reported the observance of the diamond cubic type of structure for silver iodide by the X-ray powder crystal method. The present paper reports in detail the results of an X-ray examination of a number of samples of silver iodide, some of which showed only the diamond cubic structure, while others showed a mixture of the cubic and hexagonal structures in which, as a rule, the hexagonal structure predominated. The deduction of the diamond cubic structure for silver iodide has been criticized by Aminoff and by Wyckoff, who assert that the powder method does not distinguish between the diamond, cubic, and hexagonal structures, and state that their own observations, by the Laue method, show the hexagonal form to be the true structure for silver iodide. The author points out that while the powdered crystal diffraction patterns for the two structures have many lines in common, each has lines not possessed by others, so that the powder method should distinguish between the two provided satisfactory photographs can be obtained. The powder photographs obtained in the present study show clearly the two structures, each distinguishable by its own characteristic lines. It is

² Communication No. 182 from the Research Laboratory of the Eastman Kodak Company and published in *Photo. J.*, July, 1923, p. 334.

³ Communication No. 184 from the Research Laboratory of the Eastman Kodak Company and published in *Phil. Mag.*, July, 1923, p. 487.

concluded that the disagreement among different observers is due rather to the samples examined than to the methods of analysis employed. In addition, the lattice constants of silver chloride, silver bromide and metallic silver were remeasured. The results are summarized in the following table:

Crystal.	Lattice structure.	Side of elementary unit of structure in Ångströms.	Distance apart of nearest atomic centres.
Silver chloride	Simple cubic Na-Cl type	5.540	2.770
Silver bromide	Simple cubic Na-Cl type	5.768	2.884
Silver iodide	Diamond cubic Zn-S type	6.493	2.812
Silver iodide	Hexagonal Zn-O type	4.593 ($c/a = 1.633$)	2.813
Metallic silver	Face centred cubic	4.078	2.884

A LABORATORY FRACTIONATING COLUMN.⁴

By H. T. Clarke and E. J. Rahrs.

A FRACTIONATING column constructed entirely of glass tubing arranged with suitable indentations. A cooling unit at the head provides for the desired amount of return flow. Experimental figures show that about half of each component of an equal mixture of benzene and toluene can be obtained nearly pure on the first distillation.

DEVELOPMENT OF MOTION PICTURE FILM BY THE REEL AND TANK SYSTEM.⁵

By J. I. Crabtree.

THIS article deals exhaustively with the handling of motion picture film by the reel and tank systems during the operations of developing, fixing, washing, and drying. The information is classified as follows:

⁴ Communication No. 167 from the Research Laboratory of the Eastman Kodak Company and published in *Ind. Eng. Chem.*, April, 1923, p. 349.

⁵ Communication No. 187 from the Research Laboratory of the Eastman Kodak Company and published in *Trans. Soc. Mot. Pict. Eng.*, May, 1923, p. 163.

(1) *Apparatus*.—The various types of racks, reels, tanks, and troughs are described and illustrated, the layout of a typical development room is given and the materials suitable for construction of such apparatus are discussed.

(2) *Chemical Solutions*.—Developing and fixing solutions are discussed in respect to their preparation, photographic properties, life, and methods of revival. Formulas, which fulfill the various requirements, are given.

(3) *Manipulative Details*.—Detailed instructions are given for dealing with various types of motion picture film, together with the control tests and variations in treatment under different conditions.

(4) *Troubles*.—Troubles which are commonly met with in each process are listed with suggestions for their prevention and removal.

NOTE ON THE THEORY OF PHOTOGRAPHIC SENSITIVITY.*

By S. E. Sheppard and E. P. Wightman.

THE theory that the latent image consists of colloidal silver and that there are, also, present in the grain, prior to exposure, colloidal silver specks, which form development centres by exposure, are discussed, and experimental evidence is given that such preëxistent specks do occur and that they are distributed both inside the grain as well as on the surface. It is supposed that the first action of the light is to release a photo-electron from the colloid silver speck, that the free electron, having a free kinetic energy $\frac{1}{2}mv^2 = h\nu$, where ν is the frequency of the active light, is then able to enter the silver ion, forming a neutral silver atom, while the unneutralized bromide ion loses an electron. This chain reaction, analogous to that suggested by Bodenstein, for the action of light on hydrogen and chlorine, would go on to a limiting state, depending on the initial energy of the photo-electron, but producing a nucleus large enough to initiate development for a developer of given reduction potential.

* Communication No. 185 from the Research Laboratory of the Eastman Kodak Company and published in *Science*, August 3, 1923, pp. 89-91.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

NUTRITIVE VALUE OF MIXTURES OF PROTEINS FROM CORN AND VARIOUS CONCENTRATES.¹

By D. Breese Jones, A. J. Finks and Carl O. Johns.

[ABSTRACT.]

MIXTURES consisting of 25 parts of tomato-seed press cake, soy-bean flour, or peanut flour, and 75 parts of yellow corn-meal, which contained from 12 to 15 per cent. of protein, furnished proteins adequate for the normal growth of albino rats when incorporated in a diet made nutritionally adequate with respect to the dietary factors other than protein.

A mixture of equal parts of corn-meal and coconut-meal at a protein level of 12 per cent. was efficient for growth at the normal rate. The growth was somewhat subnormal when the proportion of protein was reduced to 9.6 per cent.

From experiments in which the mixtures of corn-meal and concentrates furnished 7.2 per cent. of protein, it is concluded, from the gain in weight per gram of protein consumed, that the comparative growth-promoting value of the proteins of tomato seed, peanut, and soy bean, as a supplement to corn proteins, is in the order : Soy bean, peanut, and tomato seed.

FLUORO-ACETYL DERIVATIVES OF SUGARS.

II. OPTICAL ROTATION AND ATOMIC DIMENSION.²

By D. H. Brauns.

[ABSTRACT.]

IN comparing the optical rotations of monohalogen acetyl derivatives of glucose, cellose, xylose and fructose, the differences F-Cl, Cl-Br, and Br-I are found to be approximately proportional to the differences in atomic diameter recorded by Bragg. It is remarkable that this simple relation holds for the specific but not for the molecular rotation. The method of preparation, properties, and analyses of fluorotetra-acetyl-fructose and bromotetra-acetyl-fructose are given.

* Communicated by the Chief of the Bureau.

¹ Published in *J. Agr. Res.*, **24** (June 16, 1923) : 971.

² Published in *J. Am. Chem. Soc.*, **45** (Oct., 1923) : 2381.

IS GASEOUS NITROGEN A PRODUCT OF SEEDLING METABOLISM?³

By Jehiel Davidson.

[ABSTRACT.]

WHEAT seedlings and cow-pea seedlings were grown in Kjeldahl flasks under sterile and non-sterile conditions. The results showed that no nitrogen in gaseous form is lost in the process of germination and in the early life of the seedlings as an inherent function of their metabolic processes.

THE RELATION OF THE OXIDIZABILITY VALUE AND THE AMINO AND AMMONIA NITROGEN CONTENT TO THE QUALITY OF CREAM AND BUTTER.⁴

By L. W. Ferris.

[ABSTRACT.]

AN examination of representative samples of cream and butter from thirteen creameries showed that the second-grade cream contained a higher percentage of the total nitrogen present as amino nitrogen and ammonia than the first-grade cream. This value averaged from 1.6 to 9.6 on cream producing first-grade butter and 8.1 to 12.6 on cream producing second-grade butter. The results on the corresponding butters varied from 0.8 to 6.3 for the first-grade and from 4.7 to 6.7 for the second-grade samples. The butter from the cream containing the smaller amounts of amino nitrogen and ammonia as per cent. of the total nitrogen scored from 93 to 94, while the butter from the cream having the higher value showed a general decrease in score. The oxidizability value varied from 0.4 to 6.7 on the first-grade butter and from 3.4 to 8.8 on the second-grade butter, being higher, in general, on samples having the lower scores. Eleven authentic samples of fresh milk from individual cows gave values for amino nitrogen and ammonia as per cent. of the total nitrogen varying from 2.2 to 3.6.

³ Published in *Botan. Gaz.*, 76 (Sept., 1923) : 95.

⁴ Published in *J. Dairy Sci.*, 6 (Sept., 1923) : 412.

FURFURAL FROM CORNCOBS.⁶

III—EFFECT OF CATALYSTS ON FURFURAL YIELD IN THE STEAM DIGESTION PROCESS.

By Frederick B. LaForge and Gerald H. Mains.

[ABSTRACT.]

LABORATORY experiments were made to determine the effect of using small quantities of catalysts. With hydrochloric, sulphuric, and phosphoric acids a marked increase in the yield of furfural was obtained when the quantities of acid added were sufficient to neutralize the natural base of the cobs. Larger quantities did not give a proportionate increase. The effect of the mineral acids is probably due largely to the organic acids, especially formic, which are liberated. Direct addition of formic acid produced a somewhat greater increase in yield than did the mineral acids. Sulphurous acid gave results comparable with those obtained by formic acid, indicating that the presence of a reducing agent increases the yield. From an economic standpoint the sulphuric and sulphurous acid catalysts seem to offer the greatest promise.

Semi-commercial runs using the sulphuric acid catalyst gave furfural yields of about 9 per cent., 50 per cent. higher than those obtained in steam digestion without catalysts. The small quantity of acid used does not require neutralization, and there is no increase in steam requirement for the process. Hence the catalytic process offers a decided commercial advantage.

The Electrical Resistance to Currents of High Frequency Shown by Wires that are Enclosed in Conducting Envelopes. F. TRAUTMANN. (*Ann. d. Physik*, 1923, No. 17.)—The wires investigated were either stretched along the axes of glass tubes, filled with electrolytes, or were covered with a layer of another metal. Wave-lengths from 50 to 1800 metres were used. It should be remembered that with electric waves of high frequency the "Skin Effect" is much in evidence, that is, the current is mostly in the outer portions of the wire, while the core of the wire does little in the way of conducting current.

"Thin layers of small conductivity (electrolytes) produce considerable increases of resistance only when short waves are used, but thick layers have a bad effect even with longer wave-lengths." A case is cited (the diameter of the wire seems to be given incorrectly)

⁶ Published in *Ind. Eng. Chem.*, 15 (Oct., 1923): 1057.

where a thickness of .82 centimetre of concentrated NaCl solution around the wire caused the apparent resistance of the latter to become 5.46 times as great as the resistance had previously been for the naked wire with the same wave-length of 50 metres. When the thickness of the electrolyte was .18 centimetre the increase of resistance amounted to no more than 7.2 per cent.

Brass wires, covered with the better conductor, copper, show a better conductivity than without the copper. There is nothing odd in this, since the oscillating currents are largely in the outermost layer.

Interesting observations were made with iron and steel wire covered with a layer of copper. "The transfer of the main conductivity to the covering was in evidence even with thin layers of it. For a range of thickness of the copper the resistance of the composite wire was only slightly dependent on the wave-length used." It would thus seem possible to select ferromagnetic wire of appropriate quality and to plate with a good conductor with the result that the wire thus prepared should be much larger than the wire usually counted to be free of the skin-effect and at the same time should have a practically constant resistance for a considerable range of wave-lengths.

The author suggests that much copper can be saved by the use of iron or steel wire, copper plated, that is designed so as to have the same resistance as solid copper wire. For a wave-length of 50 metres a solid copper wire of .1025 centimetre radius has a resistance of .109 ohm per metre. The same resistance is got by using an iron wire of radius .0985 centimetre coated with copper .004 centimetre in thickness.

Copper wire plated with iron shows a great increase of resistance with frequency. Moreover, for short wave-lengths there is an enormous increase of resistance produced by a very small increase in the thickness of the iron.

G. F. S.

A New and Simple Law in the Geometrical Optics of Lenses.
E. SCHWARCZ. (*Zeit. f. Phys.*, Vol. 16, July, 1923.)—For central rays traversing a thin lens the following relation is deduced: The locus of the images of a fixed luminous point, which are produced by a lens translated along its optical axis, is a hyperbola. If the origin of coördinates is at the intersection of the optical axis with a line perpendicular to it and at a distance of twice the focal length from the object, then the hyperbola is asymptotic to the optical axis and to a second line passing through the origin. This line makes with the axis an angle determined by the fact that its tangent is the distance of the object from the axis divided by the focal length of the lens. For converging lenses the hyperbolic locus of real images lies on the side of the lens away from the object, while the locus for virtual images is on the same side. The two parts are, of course, the branches of the same hyperbola.

G. F. S.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, November 21, 1923.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, November 21, 1923.

MR. W. C. L. EGLIN, Vice-president, *in the Chair.*

The Board of Managers submitted their report. The report recorded the election of the following Life Member:

Henry Clay Gibson, Esq.,
Treasurer, Bank of North America and Trust Company,
Philadelphia, Pennsylvania;

the following Resident Members:

Dr. Arthur Howell Gerhard,
Manufacturer and Instructor in Medicine,
1615 North Delaware Avenue,
Philadelphia, Pennsylvania.

Irvin Kline Giles, Esq.,
3144 Passyunk Avenue,
Philadelphia, Pennsylvania.

Dr. Jessie A. Rodman,
Teacher of Physics,
81 High Street, Germantown,
Philadelphia, Pennsylvania.

Dr. Frederick Hollister Safford,
Professor of Mathematics,
College Hall, University of Pennsylvania,
Philadelphia, Pennsylvania.

Alfred J. Vollrath, Esq.,
Vice-president, Baker Perkins Company,
Philadelphia, Pennsylvania.

Howard Waldo Welles, Esq.,
Mechanical Engineer, Commercial Truck Company,
Philadelphia, Pennsylvania;

the following Non-resident Members:

Dr. Ellwood Hendrick,
Chemist and Author,
139 East Fortieth Street,
New York City, New York.

Dr. Louis Alexander Parsons,
Professor of Physics, Gettysburg College,
Gettysburg, Pennsylvania.

Francis du Pont Thomson, Esq.,
Engineer,
514 Yale Avenue,
Youngstown, Ohio;

the following Associate Member:

Charles Frederick Kellers, Esq.,

Student, Union College,

Schenectady, New York.

and additions to the library by gift, 23 volumes, 112 pamphlets, and by purchase, 53 volumes.

The Chairman recognized Mr. Fulweiler, who offered the following resolution, which was duly seconded and passed unanimously:

"Resolved, That a committee of three be appointed to nominate Officers and Managers for the year 1924."

The Chairman then announced that the next business of the meeting would be the presentation of the Elliott Cresson Medal to Albert Kingsbury, for his invention of the "Kingsbury Thrust Bearing," and recognized Mr. W. H. Fulweiler, Chairman of the Science and Arts Committee.

Mr. Fulweiler said: "Mr. President, Members of The Franklin Institute, Ladies and Gentlemen:

"As a nation, we have been criticized for not developing to a greater extent our resources in water power. This, however, is probably due to our economic conditions where coal has been relatively cheap and capital relatively dear.

"In the design and development of apparatus, however, our engineers have been in the forefront, and the subject of this award has to do with the development of an important feature in the construction of large turbine units. One of the factors which has appeared to limit the construction of larger turbines was the difficulty of properly lubricating the thrust bearings which were called upon with the enlargement of the apparatus to carry tremendous loads.

"Various devices were employed to secure the necessary lubrication, among these being the supplying of oil under very high pressure but with any failure of the oil supply the unit naturally had to be shut down. In Mr. Kingsbury's invention the bearing is composed of a solid upper plate supported by a number of segments or shoes. The whole bearing is immersed in a bath of oil. In order to insure the entrance of the oil between the bearing surface the thrust pressure is not transmitted to the separate shoes in the centre of their areas but slightly eccentrically, so that as the upper plate revolves a wedge-shaped film of oil is continuously dragged between the bearing surfaces. In this manner, ample and adequate lubrication is always secured without the dependence upon external auxiliary such as oil pressure pumps, etc.

"This invention has been applied not only to thrust bearings on large turbine units, but also to ship propellers and a large number of our destroyers are equipped with this type of bearing.

"Your Committee on Science and the Arts, through a sub-committee, has very carefully examined this invention, and their report concludes as follows:

"In consideration of marked excellence of design and construction and signal success in eliminating end thrust troubles from modern high-power turbine machinery, The Franklin Institute awards its Elliott Cresson Medal to Albert Kingsbury, Esq., of Philadelphia, Pennsylvania, for his Thrust Bearing."

" Mr. President, I have the honour to present to you Mr. Albert Kingsbury, of Philadelphia, to receive the Elliott Cresson Medal for his invention of the Thrust Bearing."

The Chairman presented the medal and accompanying documents to Mr. Kingsbury, who expressed his appreciation of the high honour conferred upon him by the Institute.

The Chairman also announced that the Edward Longstreth Medal would be presented to Harry S. Parks for his invention of the " Pnumercator Tank and Draft Gauge " and again recognized Mr. Fulweiler.

Mr. Fulweiler said: " Mr. President, Members of The Franklin Institute, Ladies and Gentlemen :

" One of the most important developments in the operation of vessels has been the use of oil fuel. This has been especially important for naval vessels and for the faster passenger ships. The great advantage of oil fuel is the fact that it requires less space for its storage, thus permitting greater cruising radius or greater cargo space at the same time reducing the fire room force.

" Another reason why oil fuel may be so advantageously used is the fact that it can be stored in almost any available space, for instance, double bottoms may be used or one tank may be placed above another. It is necessary, however, to have means to measure the contents of these tanks and it must be evident that frequently the tanks must be placed in relatively inaccessible positions. The invention of Mr. Parks has to do with the most ingenious method which he has devised for measuring the contents of tanks which may be in any position. It is only necessary that the actual measuring apparatus which consists of a mercury gauge supplied with compressed air be connected to the tank by means of a thin copper tube not so large as a lead pencil.

" In the operation of the device, air is passed into the apparatus until the hydrostatic head due to the material in the tank is balanced against the mercury gauge, thus by means of appropriate calibrations the contents of the tanks may be read directly.

" It is natural that such an ingenious device would find a number of applications, among these might be mentioned its use in determining the draft of vessels and by combining the draft forward and aft with appropriate calibration of the gauge, the dead-weight tonnage of the vessel may be determined at any time or again by determining the draft at two points located in a horizontal plane, the trim of the vessel can be determined. This device has also been applied to the measurement of oil in numerous tanks, all of the readings being made from a central point.

" Your Committee on Science and the Arts has very carefully investigated Mr. Parks' invention and in consideration of soundness in design, excellence of construction, and its proved value as a practical indicating device for the distant measurement of liquid pressure, The Franklin Institute awards its Edward Longstreth Medal to Harry S. Parks, Esq., of Philadelphia, Pennsylvania, for his Pnumercator Tank and Draft Gauge.

" Mr. President, I have the honour to present Mr. Harry S. Parks to receive the Edward Longstreth Medal for his invention of the Pnumercator Tank and Draft Gauge."

The Chairman presented the medal and accompanying documents to Mr. Parks, who thanked the Institute for the honour conferred upon him.

The Chairman then introduced Rear-Admiral William A. Moffet, U. S. N., Chief, Bureau of Aeronautics, Navy Department, Washington, D. C., who presented the paper of the evening on the "ZR-1, the First Helium-filled Dirigible."

The speaker referred to the cessation of airship building abroad and to the reviving of this art by the American Navy, which constructed the ZR-1, in which is used helium, a non-combustible and non-explosive gas. By use of lantern slides, he pointed out the main structural members of this airship, the arrangement of the gas bags and the location of the motors. He said that naval constructors had turned their hands to airship building, and were pioneering for a new industry and a new commercial era in aeronautics. He further referred to the airship as a new factor in world commerce, and by use of charts pointed out possible airship routes which would greatly aid in speeding up communications and cutting down distances. He also emphasized the great importance and value of the airship as a naval unit.

After a brief discussion, a rising vote of thanks was extended to the speaker, and the meeting adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

*(Abstract of Proceedings of Stated Meeting held Wednesday,
November 7, 1923.)*

HALL OF THE INSTITUTE,
PHILADELPHIA, November 7, 1923.

MR. W. H. FULWEILER, *in the Chair.*

The following report was presented for first reading:

No. 2792: Mills-Packard Patent Water-cooled Chambers for the
Manufacture of Sulphuric Acid.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, November 14, 1923.)

RESIDENT MEMBERS.

DR. ARTHUR HOWELL GERHARD, Manufacturer and Instructor in Medicine, 1615
North Delaware Avenue, Philadelphia, Pennsylvania.

MR. HENRY CLAY GIBSON, Treasurer, Bank of North America and Trust
Company, Philadelphia, Pennsylvania.

MR. IRVIN KLINE GILES, in care of Atlantic Refining Company, Philadelphia,
Pennsylvania.

DR. JESSIE A. RODMAN, Teacher of Physics, 81 High Street, Germantown,
Philadelphia, Pennsylvania.

- DR. FREDERICK HOLLISTER SAFFORD, Professor of Mathematics, College Hall, University of Pennsylvania, Philadelphia, Pennsylvania.
- MR. ALFRED J. VOLLRATH, Vice-president, Baker Perkins Company, 661 Drexel Building, Philadelphia, Pennsylvania.
- MR. HOWARD W. WELLES, Mechanical Engineer, Commercial Truck Company, Philadelphia, Pennsylvania.

NON-RESIDENT MEMBERS.

- MR. WILLIAM DUBILIER, President, Dubilier Condenser and Radio Corporation, 48 West Fourth Street, New York City, New York.
- DR. ELLWOOD HENDRICK, Chemist and Author, 139 East Fortieth Street, New York City, New York.
- DR. LOUIS ALEXANDER PARSONS, Professor of Physics, Gettysburg College, Gettysburg, Pennsylvania.
- MR. IOWA SMITH, Commercial Engineer, International Telephone Company, Clinton Building, Columbus, Ohio.
- MR. FRANCIS DU PONT THOMSON, Engineer, 514 Yale Avenue, Youngstown, Ohio.

ASSOCIATE MEMBERS.

- MR. CHARLES FREDERICK KELLERS, Student, Union College, Schenectady, New York.

CHANGES OF ADDRESS.

- MR. C. E. BENNETT, Electrical Engineer, Georgia Railway and Power Company, Atlanta, Georgia.
- MR. ARTHUR BLACKBURN, 405 Hollen Road (Cedarcroft), Baltimore, Maryland.
- MR. ERNEST H. DAVIS, 901 Vine Avenue, Williamsport, Pennsylvania.
- MR. FRANK GITTELSON, 1017 Spruce Street, Philadelphia, Pennsylvania.
- PROF. MOSES GOMBERG, 712 Onandaga Street, Ann Arbor, Michigan.
- MR. EDWARD HEITMAN, 630 Bergen Avenue, Jersey City, New Jersey.
- MR. F. E. IVES, 1726 North Park Avenue, Philadelphia, Pennsylvania.
- DR. ENOCH KARRER, National Lamp Works of General Electric Company, Wire Division, Cleveland, Ohio.
- MR. LEONARD KEBLER, 21 Ridge Road, Bronxville, New York.
- MR. THADDEUS MERRIMAN, Chief Engineer, Board of Water Supply, Municipal Building, New York City, New York.
- MR. B. B. MILNER, Room 1237, Knickerbocker Building, Times Square, New York City, New York.
- MR. W. E. MOORE, President, W. E. Moore and Company, Engineers, 706 Union Bank Building, Pittsburgh, Pennsylvania.
- MR. WALTER RAUTENSTRAUCH, Vice-president and General Manager, Liberty Yeast Corporation, 56 West Forty-fifth Street, New York City, New York.
- MR. ROBERT RIDGWAY, Chief Engineer, Transit Commission, State of New York, 49 Lafayette Street, New York City, New York.
- MR. W. S. RUGG, University Club, Natalie Street, Pittsburgh, Pennsylvania.
- MR. GEORGE SATTERTHWAITE, in care of Henry Disston and Sons, Tacony, Philadelphia, Pennsylvania.

- MR. J. WALDO SMITH, Consulting Engineer, Board of Water Supply, Municipal Building, New York City, New York.
 LT. COL. H. S. SPACKMAN, Egypt Mills Post Office, Pike County, Pennsylvania.
 LT. COL. FRED. H. WAGNER, Tuscany Apartments, Thirty-ninth Street and Stony Run Lane, Baltimore, Maryland.
 MR. ARTHUR M. WILSON, 434 Walnut Street, Philadelphia, Pennsylvania.

NECROLOGY.

- MR. F. J. Cole, 640 South Hill Avenue, Pasadena, California.
 Dr. Charles P. Steinmetz, Wendell Avenue, Schenectady, New York.
 Mr. Philip Nell, 3619 North Marshall Street, Philadelphia, Pennsylvania.

LIBRARY NOTES.

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BOOK REVIEWS.

TECHNICAL METHODS IN ANALYSIS OF METALLURGICAL AND ALLIED PRODUCTS.
By Wilfred W. Scott, Sc.D., Colorado School of Mines. xxviii-875 pages.
8vo. 150 illustrations and 2 colored plates. New York, D. Van Nostrand
Company, 1923. Price, \$6 net.

In preparing the present work the author has had in mind the combining of a manual for students in advanced courses and a reference for the practising metallurgist. With eight years of experience as a teacher of chemistry and twelve years as a professional metallurgist, the author is well equipped to

meet these two tasks, nevertheless, specialism has gone so far in chemistry, as in every other science, that collaborators have been necessary. These collaborators are Doctor Van Tuyl, Doctor Palmer and Doctor Low, colleagues of the author, and Doctor Hale of the Department of Water Supply, Gas and Fuel of New York City. The table of contents covers twenty-one pages, the items being set forth in unusually extended form. It is a question if this is necessary. A good index is far more serviceable. A book of this character will find its largest use as a reference, and the quick finding of a given item is what the user desires. A full list of illustrations is also given. This also seems unnecessary. It would probably be regarded as inadvisable to include the illustrations in the index, but it seems to the reviewer that such an arrangement would be as satisfactory as the separate list, and even more satisfactory than a list in which the arrangement is by order of pages. In this latter arrangement one has to know where the illustration is in order to turn to it quickly. Indeed, a consultation of the index shows that the illustrations are, at least in some cases, included.

The book presents a great variety of processes. The specific descriptions are preceded by a comprehensive chapter on analytic methods, including instruction in the principal phases of stoichiometry. A justifiable note is given to the student that it is usually unnecessary to carry calculations beyond the second decimal place. The practice of carrying to four or five places has, indeed, disappeared. Older chemists can remember the absurd practice, especially in vogue among German chemists, in which the data in water analysis were expressed to four or five decimal places, and this when the atomic weights were not accurately determined beyond the first decimal.

The work is rather liberally illustrated, but in a number of cases these are merely cuts from catalogues. It is doubtful if either student or practising analyst gets any benefit or finds any interest in a picture of a drying oven or an analytic balance. Actual use of the apparatus is the method of acquiring a knowledge thereof. The analytic balance illustrated is one furnished by a special supply company, but many analysts will from necessity or choice use other types. The same is true of the picture of the set of weights. It means nothing to anyone. There are two colored plates, one of arsenic stains under Gutzeit's method, the other of spectra, the latter by a typographical error being entitled "Emmissions-spectra," which gives rise to a suspicion that it was "made in Germany." In these cases also, the reviewer is of the opinion that the expense involved in such printing is not necessary. Students should be made familiar with spectra and the whole range of color reactions by actual experience. A few hours spent with a good spectroscope and carefully selected substances are more useful than the best plates that can be produced.

Doctor Scott's book, however, does not suffer in value and usefulness by these accessory matters. He has combined in it a very large amount of information in the field of metallurgical analysis. In this field the time-element has come to be of great importance. Formerly, the analysis of ores and metals was mostly the work of those regularly engaged in general practice. The days when the chemist was toxicologist, sanitarian and metallurgist are gone, and the large industrial establishments have their own laboratories. Gone also are the days when twenty-four or forty-eight hours could be allowed for

a determination of sulphur in a coal or copper in an ore. To-day rapid methods are needed. The introduction of analyzed reagents and standard methods has simplified and speeded up the works-laboratory as well as that of the professional analyst. The book in hand will be of great aid to both classes of chemists.

HENRY LEFFMANN.

L'INDUSTRIE DU GAZ. DISTILLATION DE LA HOUILLE. By René Masse and Auguste Baril. 295 pages, 77 illustrations, small 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, in paper, 20 Francs, net.

TRAITEMENT DES PRODUITS ET SOUS-PRODUITS. By the same authors. 307 pages, 115 illustrations, small 8vo. By the same publishers, 1923. Price, paper bound, 20 Francs, net.

These volumes are part of the second series of the *Encyclopédie Léauté*, conducted by André Léauté, which is intended to present compact, up-to-date information on basic chemical industries. The two volumes comprise the whole field of chemical engineering in regard to the products of the distillation of coal. They contain a very large amount of information and are evidently the work of experienced gas engineers. The French word "houille" is, according to Littré, of unknown etymology; it has recently come into prominence in connection with the expressive French term for water power "houille blanche," "white coal." The first of the two volumes is devoted to the methods of distilling coal for obtaining illuminating gas. The descriptive text is preceded by a short history of illumination, and specifically of the beginning of the use of gaseous materials. We are not surprised that the authors claim the first step in this direction to have been made by a Frenchman, but they seem to make out a case for Lebon, who in 1787 experimented on the distillation of sawdust on a very small scale. His early death prevented extended development of his views. Reference is, of course, made to the part taken by Murdoch in the practical application of coal-gas.

The question of the possible ousting of gas lighting by electric lighting is discussed briefly. The authors are enthusiastic in their view that no such danger impends at present. "Il n'en est rien," "nothing doing," is their verdict. The matter is hardly to be dismissed so easily. It does not follow, however, that if gas lighting should become uncommon, that the gas-making industry would suffer serious injury. Modern invention has shown its very useful adaptation to fields entirely outside of lighting. Cooking by gas, and limited heating of rooms has been long in vogue, and as the coal problem becomes more and more serious, as it is almost sure to do, the usefulness of gaseous fuel will be enhanced. Gas engineers and experts in public utilities should turn actively towards the problem of adapting ordinary gas to general house heating. At present the so-called stoves for room heating are wasteful and unsanitary. It seems entirely probable that a careful study of the subject will result in the invention of stoves which are economical, safe and ornamental. If the illuminating phase is entirely surrendered to the electric company, it will be possible to avoid the cost of enriching the low candle-power products, such as pure water gas, and to serve the gas as made, but in such case a stench must be inserted to protect against accidental escape. One of the United States scientific bureaus has been giving a great deal of attention

to the question of suitable stenches. Messrs. Masse and Baril are of the opinion that electric and gas companies should combine, a thought with which most persons will agree.

Valuable information is given concerning the distribution of gas-coal in the world. The United States is one of the most abundantly supplied. The authors remark that the United States has been wasting its resources in this respect—as indeed, it has been doing in many other respects—but is now proceeding more carefully. Some note is made of the destruction of the mines in the part of France occupied by the Germans. The figures showing the rehabilitation of these are encouraging. In January, 1919, only about 1500 tons (presumably metric tons) were produced, but in January, 1923, considerable over 800,000 tons.

The two books cover together all the important principles involved in gas engineering and by-product handling, and are well worth the attention of engineers in that field.

HENRY LEFFMANN.

VALENCE AND THE STRUCTURE OF ATOMS AND MOLECULES. By Gilbert Newton Lewis, University of California. American Chemical Society Monograph Series. 172 pages, 27 illustrations, 8vo. New York, Chemical Catalog Company, Inc., 1923. Price, \$3 net.

This is a profound, but clearly set forth, study of the most recent developments in the field of atomic and molecular physical chemistry. The author expresses in the preface that the data, or at least the inferences here presented, belong to the ephemeral literature of the science. If this is true, and the reviewer is not inclined to dispute it, the same may be said for all inferences in all sciences. The progress of knowledge may be compared to the ascending of a spiral staircase. The observer stops at a certain point and views the landscape. His view is bounded by a horizon either far away or limited by hills or forest. He travels on and soon arrives at the opposite point of the circle. The whole view has changed. Nature does not present the same aspects and he revises his inferences. Still travelling he arrives at the same point of the circle from which he started, but a little higher up. A more distant horizon is observed. The older inferences return but with modifications. Thus science moves. Ideas are accepted; theories and hypotheses become dominant; the competence of teachers and workers is tested by the extent to which they accept the dogmas. Research moves on, theories and hypotheses are thrown aside, but later rescued, modified and again set up for worship. Professor Lewis seems to hold the same thought but believes in a more rapid change, comparing the progress of science to the views in a kaleidoscope. He has been active in research in the field to which this work is devoted and is competent to speak on every phase of it. He has given chemists an interesting and valuable condensation of the recent literature.

The opening chapter is appropriately a historical summary, beginning with Dalton's theory. That matter is discrete was held by Greek philosophers, but unfortunately we have only scanty reference to them in quotations in writings of much later date. Naturally, the atomic theory when generally received led to speculations as to the possible unity of matter, that is, that all elements are but modifications of one form. In the middle of the nineteenth

century such speculation was quite popular; enthusiastic believers in it went so far as to give a name—protyle—to the primordial element. The exact determination of atomic weights showing many fractional numbers, the decimals of which could not be ascribed to errors of method, caused the abatement of the theory, which had been due mainly to Prout, and until the discovery of the remarkable transmutability of radio-active elements, chemists gave little thought either to the old alchemical visions of transmutation or to the hypothesis of an "Urstoff." Now the world has moved around to the old position on the staircase, but somewhat higher in level, and the isolation of isotopes has brought Prout's view more into consideration. After all, is not the evolution of matter as probable as the evolution of the objects which matter constitutes? The doctrine of the evolution of living forms is ancient, but the presentation of it with the evidence for its truth is due mostly to Darwin. His view on natural selection underwent a period of retrogression; it was considered good form to deprecate it, but at present naturalists seem to be returning to it.

Professor Lewis has given to chemists, physical chemists and physicists a valuable contribution, for he has summarized and vividly presented to most recent results and inferences in the field of atomic and molecular structure. Some of the older workers, and the more conservative, may, indeed, smile or even be irritated at the complication involved in the presentation of the structure of some simple molecules, but the evidence is at hand and the present-day teacher cannot afford to overlook these views. The book, as usual in the series to which it belongs, is well printed and up to date. HENRY LEFFMANN.

CHEMISCH-TECHNISCHE VORSCHRIFTEN. By Otto Lange, Technical High School, Munich. Third edition, enlarged and thoroughly revised, Vol. 2, Fasern, Massen und Schichten. xix-806 pages, 8vo. Leipzig, Otto Spamer, 1923. Price \$8.35 net.

The general character of this work was set forth in a review of the first volume in the issue of this JOURNAL for September last. The work is to be in four volumes, and it is obvious, from the contents of the first two, that when completed it will be one of the most comprehensive and complete summaries of industrial chemistry in any language. The present volume deals with manufactured articles, mostly organic that are used in the form of fibers, sheets or masses of moderate size. Under the latter term—"Massen" in the original—are included leather, natural and artificial, bone, horn and sponge products, celluloid, adhesives, plastics, peat, sawdust, casein products, and many other more or less analogous materials. The section on fibers includes extensive treatment of paper, all forms of wood-fibers, artificial fibers, and the several forms of cellulose esters. Vegetable and animal fibers are, of course, extensively treated. In the section on sheets, sensitive films are described together with photographic processes, even the sources of light and the nature of light filters and screens are discussed. It is quite impossible in the space available to do more than indicate in outline the merits of this work. The amount of material collected is immense, and the copious references to patent and journalistic literature extend greatly the serviceability of the book. As stated in the review of the first volume, no narrow nationalism restricts Doctor Lange's view of chemistry. As in the first volume, the index references are

to paragraphs, not to pages, a method that at first embarrasses the American user, but this difficulty soon disappears. On the relative merits of page and paragraph reference much discussion might arise. The reviewer is strongly in favor of the former common and long-established method, but the other is not seriously objectionable. The index is very elaborate, and this is not the least commendable point in the book. The volume in hand sustains the position accorded to the first volume, and the work is undoubtedly one of the most valuable in the field to which it is devoted. The appearance of these extensive and excellent books must be considered evidence that along some lines, at least, Germany is rapidly recovering from the effects of the war.

HENRY LEFFMANN.

THE HANDBOOK OF INDUSTRIAL OIL ENGINEERING. By John Rome Battle, B.S. in M.E., M.E. Second edition, revised, 1141 pages, 100 line drawings, over 200 half-tones, 9 colored plates and many other illustrations, 9 charts, 8vo. Philadelphia, J. B. Lippincott Company, 1923. Price, \$10. net.

The first edition of this book met a great want in engineering and was soon exhausted. The author has taken the opportunity to thoroughly revise and extend the work so as to bring it up to date. The mere enumeration of the subjects included would fill a large space. On account of this comprehensiveness, the book will find application in all the fields of oil engineering and be a valuable reference work for all persons associated with the manifold uses in which oil is now employed. The volume in hand is, indeed, only one portion of the work, being the section devoted to lubricating and industrial oils.

The enormous number of illustrations constitute in themselves a vivid picture of the importance and extent of the use of oils. Over a hundred useful tables are included. It is a reference book of data, relating to lubrication and industrial oils, including tables, general oil information, engineering and industrial requirements, for the use of oil engineers, lubricating engineers, oil salesmen, oil equipment manufacturers, mechanical engineers, machinery designers, mill and power plant superintendents, and others interested in the efficient utilization of oil products and equipment, and the conservation of power.

The mechanical construction of the book is excellent, and a comprehensive index will greatly aid the user.

HENRY LEFFMANN.

MANIPULATIONS DE CHIMIE COLLOÏDALE. Par Wo. Ostwald. Translated by Edmond Vellinger, with permission of the author. 201 pages, 21 illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1924. Price, 10 Francs.

This being a translation from a standard work, that has already gone through four editions in its original language, requires little more than the announcement of publication. The book contains a large number of directions for obtaining colloids and demonstrating their properties. The part played by chemistry in many sciences is widening steadily, and chemical principles and methods find application in many ways, especially in physiology, biology and medicine. New methods must be employed with a knowledge of the mechanisms involved, as far as these can be ascertained. The translator has done good service to French chemists by rendering this book into their language. Beginners in the study of colloid chemistry will find it of great value. The translation carries the first and fourth prefaces of the German work. In the latter,

the author states that some reviewers have suggested that an index should be added, but he has deliberately declined, inasmuch as the table of contents is elaborate and will answer all purposes. This attitude is to be regretted. As might be expected, with this example before him, the translator has not supplied an index.

HENRY LEFFMANN.

PUBLICATIONS RECEIVED.

Chemisch-Technische Vorschriften. Ein Handbuch der speziellen chemischen Technologie von Dr. Otto Lange. Dritte, erweiterte und völlig Neubearbeitete Auflage. II Band, Fasern, Massen und Schichten. 806 pages, 8vo. Leipzig, Otto Spamer, 1923. Price, in paper, \$8.35.

Technical Methods in Analysis of Metallurgical and Allied Products. A manual of analytical methods and useful data for the chemist and the college student by Wilfred W. Scott. 875 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1923. Price, \$6.

Valence and the Structure of Atoms and Molecules. By Gilbert Newton Lewis. American Chemical Society Monograph Series. 172 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1923. Price, \$3.

The Handbook of Industrial Oil Engineering. A reference book of data, relating to lubrication and industrial oils, including tables, general oil information, engineering and industrial requirements, for the use of oil engineers, oil salesmen, oil equipment manufacturers, mechanical engineers, machinery designers, mill and power plant superintendents, and others interested in the efficient utilization of oil products and equipment, and the conservation of power, includes the lubricating engineer's handbook revised by John Rome Battle. Second edition, revised. 1141 pages, illustrations, diagrams, plates, maps, 12mo. Philadelphia, J. B. Lippincott Company, 1923. Price, \$10.

A Treatise on Engine Balance Using Exponentials. By P. Cormac. 151 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1923. Price, \$8.

Textile Chemistry. An introduction to the chemistry of the cotton industry by F. J. Cooper. 235 pages, illustrations, 8vo. New York, E. P. Dutton and Company. Price, \$5.

Cours Complet de Mathématique Spéciales. Par J. Haag. Tome IV, géométrie descriptive et trigonométrie. 152 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, 13 Francs.

Exercices du Cours de Mathématique Spéciales. Par J. Haag. Tome IV, géométrie descriptive et trigonométrie. 154 pages, 8vo. Paris, Gauthier-Villars et Cie., 1924. Price, 15 Francs.

L'Industrie du Gaz. Traitement des Produits et Sous-produits. Par René Masse et Auguste Baril. Encyclopédie Léauté. 307 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1923. Price, 20 Francs.

L'Industrie du Gaz. Distillation de la Houille. Par René Masse et Auguste Baril. Encyclopédie Léauté. 295 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1923. Price, 20 Francs.

La Lumière Monochromatique, sa Production et son Emploi en optique pratique. Par Ch. Fabry. 37 pages, illustrations, 8vo. Paris, Revue d'Optique theorique et instrumentale, 1923.

Les Applications des Interférences Lumineuses. Par Ch. Fabry, professeur a la Sorbonne. 160 pages, illustrations, 8vo. Paris, Revue d'Optique theorique et instrumentale, 1923.

Ventilation of Central Station Buildings and Equipment. A report of the sub-committee on ventilation of the Electrical Apparatus Committee. 46 pages, illustrations, quarto. New York, National Electric Light Association, 1923. Price, 40 cents.

Ontario Department of Mines. Thirty-first Annual Report, 1922. Two parts, illustrations, maps, 8vo. Toronto, King's Printer, 1923.

National Advisory Committee for Aeronautics. Technical Notes, No. 161, Preliminary Study of the Damping Factor in Roll, by Lieut. James M. Shoemaker, U. S. N. 17 pages, diagrams, quarto. No. 162, The Arithmetic of Distribution in Multi-cylinder Engines, by Stanwood W. Sparrow. 9 pages, diagrams, quarto. No. 164, General Theory of Windmills, by Max M. Munk. 5 pages, diagrams, quarto. No. 165, Tests on Riveted Joints in Sheet Duralmin, by H. F. Rettew and G. Thumin. Abstracted and revised by J. G. Lee. 5 pages, diagrams, quarto. Washington, Committee, 1923.

List of Manuscript Bibliographies in the Biological Sciences.—

This treatise has been compiled by CLARENCE J. WEST and CALLIE HULL, and published as No. 45 in the Reprint and Circular Series of the National Research Council (Washington, D. C., June, 1923, 51 pages). It includes unpublished bibliographies in the biological sciences which are available to research workers. Separate sections are devoted to biochemistry and biophysics. Many bibliographies of a distinctly chemical nature occur in other sections, such as those devoted to physiology and pharmacology. The following information is given for each bibliography: Compiler and his address, number of entries, years covered, other items of interest. Many entries in the list, such as those devoted to canned foods, insecticides, fertilizers, photosynthesis, meteorology, are of deep interest to the technologist.

J. S. H.

Identification of Amines.—C. S. MARVEL and F. E. SMITH, of the University of Illinois (*J. Am. Chem. Soc.*, 1923, 45, 2696–2698), recommended para bromobenzenesulphonyl chloride as a reagent for the identification of amines. This reagent is treated with a slight excess of the amine. If necessary, heat is applied to start the reaction. The resulting para bromobenzenesulphonamide is purified by washing with dilute hydrochloric acid, and recrystallization from alcohol of the proper concentration, and is then identified by its properties, such as its melting point and the percentage of bromine found on analysis.

J. S. H.

CURRENT TOPICS.

Platinum Conditions in 1922.—Advance sheets of the 1922 issue of the "Mineral Resources of the United States" have just been distributed by the Geological Survey. The section devoted to platinum and allied metals was prepared by J. M. Hill. The enormous advance in the price of platinum has been a serious burden upon some industries and upon chemists. The metal is practically indispensable in a few analytic operations, though fused quartz and some alloys have partly relieved the strain. For many years, manufactured platinum ware sold at retail at about three cents a grain. Crude metal in ingots was sometimes as low as \$9 per troy ounce. The principal supply was from the Urals, only small amounts coming from other sources, some South American gold occasionally yielding a little. The price began to advance about the beginning of the present century, and with slight fluctuations has steadily increased until platinum wire was lately quoted by a supply house at \$3.97 per gram, close to \$125 per troy ounce, about six times the price of gold. As soon as the price advanced materially above that of gold, jewelers began to use it, and the consumption for this purpose has contributed largely to the present exalted figure. Nearly 70 per cent. of the platinum used in the United States enters into jewelry.

The report gives no encouragement to those who are hoping for a material reduction in cost of the metal. Notwithstanding the intensive search, stimulated by the high price, no new localities of importance have been found. A promoter's boom was started in one of the western states, but soon collapsed under expert examination. The Russian field has not yet resumed active supply. In 1913, 250,000 troy ounces were furnished by it. The yield fell to one-half in 1915, and steadily decreased, until in 1921 only 20,000 ounces are credited. Colombia is now the most abundant producer, nearly 40,000 ounces having been imported into the United States in 1922. This is, of course, crude, carrying more or less of the related metals. The production in the United States is inconsiderable; only about 1000 ounces in 1922. A notable item is the use of palladium in jewelry for the manufacture of the so-called "white gold." The price of this metal has remained during the year at about \$55 per troy ounce. Iridium has risen greatly, closing for the year at \$260 per troy ounce. The customs reports for the year show no direct Russian supply, but considerable importations from Asthonia, Latvia and Sweden are believed to be of Russian origin. About 35,000 ounces credited to England and 11,400 to France are, of course, obtained from other countries, probably principally from Colombia and Russia. No definite information, however, seems to be at hand as to the extent to

which the Russian fields were worked during the period covered by the report.

The relative amounts of platinum and allied metals used in certain industries are approximately as follows:

	Per cent.
Jewelry	66.6
Electric apparatus	16.1
Dental materials	9.5
Chemical apparatus	5.2

The balance is distributed through several minor industries. The most marked increase over 1921 is in jewelry, which rose from 59.5 per cent. to the figure given above. H. L.

Notes from the Sixty-sixth Meeting of the American Chemical Society, Held at Milwaukee, Wisconsin, September, 1923.—Furfural from Corn-cobs.—Further investigation of the properties of furfural, obtained from corn-cobs, has indicated, according to the paper by Mahood and Harris, that a rich brown dye can be made from this substance. The experiments of these authors may lead to the production of an entire series of dyes in which this material is used to replace others already in use and thus in a series of dyes entirely American both as to method and materials of manufacture.

Natural Water Corrosion of Steel in Contact with Copper.—Experiments are described by Whitman and Russell wherein the natural water corrosion of steel in contact with a metal lower in the electromotive series has been quantitatively determined. The results show that the total corrosion is the same with bare steel plates as with steel specimens of the same size having 75 per cent. of their surface copper plated, *i.e.*, in the latter case the corrosion per unit area of steel is four times as great as in the former. The total corrosion observed is determined by the total effective surface available for the depolarization of hydrogen by dissolved oxygen, the actual corrosion occurring on the steel alone.

These results are not readily explainable by the colloidal theories of corrosion advanced by J. N. Fried or Bengough and Stuart, both of which agree that hydrogen is not an essential in natural water corrosion. The data are, however, in entire accord with an electrolytic mechanism of corrosion. The electrolytic theory explains these results by picturing the increased corrosion per unit area of steel as caused by the depolarization of a film of nascent hydrogen. This film is deposited on the steel and on the adjacent copper surface and its removal is affected by diffusion of dissolved oxygen into the metal. The rate of corrosion is limited by the rate at which oxygen can diffuse in to react with the surface film of nascent hydrogen.

The Rôle of Bread in Nutrition.—Worth Hale finds that the consumption of wheat products in the United States rose, in the years 1915 to 1920, from 5.3 bushels to 5.8 bushels per capita. Bread is the

chief nutrient eaten at one or more meals each day by many growing children. The nutritive quality of bread thus becomes an important factor in the growth and health of these children and, to a less extent, the health of adults.

Only one commercial white bread and no whole wheat bread, of many examined, was found to be adequate for the growth and maintenance of animals. Experimental white breads, made with the addition of the aqueous extract of wheat embryo and with a small percentage of milk, proved far superior to the average white or whole wheat bread. A commercial white bread, developed along similar lines, likewise is far superior to all breads examined, including so-called cream, vitamin, and whole wheat breads. This bread equals the growth inducing qualities of normal diets and protects animals from the development of xerophthalmia and polyneuritis. Its high value as a nutrient is further supported by children feeding tests.

H. L.

The Movement of Water in a Body Caused by Explosions in the Liquid. C. RAMSAUER. (*Ann. d. Physik.*, 1923, No. 20.)—When a charge is set off under water, a spherical wave of pressure travels outward with a speed dependent on the compressibility of water. At the same time the gases developed by the explosion push the adjacent water bodily outward. It is with this second phase of the phenomenon that the present investigation concerns itself.

The apparatus for detecting the bodily motion of the water consists of an electric circuit containing a battery, an electromagnet and connecting wires. When the circuit is closed, the electromagnet attracts its armature in opposition to the pull of a spring. The cessation of the current is followed by the release of the armature. In use the electromagnet and battery are set up on land at a safe distance, but the connecting wires, properly insulated, pass through the water to the vicinity of the explosion. There the wire is no longer continuous. It is cut and the two ends are both in the water. Sufficient current flows from one end to the other to hold the armature in place. One end of the wire, that placed nearer to the centre of explosion, is in reality merely an end of wire, while the other is expanded into a plate.

When the charge is set off, the retention of the armature indicates that water has remained between the wire and the plate. On the other hand, the release of the armature shows that the expanding gas has thrust away the water from the wire and has thus interrupted the electric circuit. A series of such pieces of apparatus, set at different distances from the explosion, will furnish information in regard to the distance through which the water is bodily pushed away by the explosion. If one armature is set free, while an adjacent one is held in position, it follows that the expanding gas reached one terminal wire but did not go far enough to reach the neighboring wire.

In the experiments the two variables introduced were the number

of grams of guncotton used and the depth of the cartridge below the surface of the water. The greatest distance outward through which the water was projected was found to be closely in proportion to the cube root of the mass of the charge divided by the pressure at the point of explosion. With the same charge of 1910 grams the water was moved outward through 166 centimetres, when the cartridge was situated three metres below the water surface, and 146 centimetres, when the depth was eight metres. Reducing the charge to 470 grams caused the distance to come down to 98 centimetres.

The same apparatus was used to measure the speed of motion of the out-thrust water. The interval between the interruption of two circuits whose wires were at different distances from the centre of explosion was recorded. The speed, as would be expected, diminished with the distance from the cartridge. At a distance of 40 centimetres it was 63 metres per second, but only 12.5 metres per second at three times the distance from the source.

G. F. S.

Coal in 1919, 1920 and 1921.—A pamphlet of 218 pages, covering pages 445 to 662 of the forthcoming volume of the report on "Mineral Resources of the United States," has just been issued under the auspices of the U. S. Geological Survey. The section has been prepared by F. G. Tyron and S. A. Hale. The United States is the greatest coal-producing and coal-consuming country in the world, and notwithstanding the extent to which its supplies have been drawn on, enormous quantities still remain and early exhaustion is not probable. The coal-mining industry has of late been subject to great interference through strikes, and disagreements between operators and workers. The work is hard and dangerous. Injuries, fatal and non-fatal, are common, and every now and then the nation is shocked by some wholesale disaster. Several types of coal are found in the country. The anthracite deposits of Pennsylvania are practically unique and constitute the best fuel for domestic use. It is, however, steadily increasing in price, although some of the smallest sizes, which are by-products of preparation for market, are in excess of demand, largely on account of the lack of furnaces suitable for use of them.

The report which suggests this note gives elaborate statistics of the production and handling of coal produced in the United States during the years 1919, 1920 and 1921, and a chart, prepared by Miss Lida Mann, shows the amounts of coal produced each year since 1807. The figures for the years 1807 to 1820 are combined. In this first period 15,000 tons were mined, of which 300 were Maryland bituminous and the rest Pennsylvania anthracite. The high-water mark for anthracite was in 1917, when nearly 100,000,000 tons were mined. The total production of anthracite to date is over 3,000,000,000 tons, and of all forms of coal over 14,000,000,000. The number of men employed in anthracite mining has fallen off somewhat; in the last year covered by the report, it was nearly 160,000. A much larger

number work in the bituminous mines, the figure for 1921 being over 660,000. The working days do not reach quite 300 for each year, the deficiencies being due to Sundays, legal holidays and certain national or religious holidays of groups of workers. Statistics of injuries in the mines are not included as these matters belong to another department.

In this connection may be mentioned a paper in the *Trans. and Proc. of the Royal Society of South Australia* (1922, 44, 131), by Sir D. Mawson and F. Chapman, on the brown coals of that region. Analysis shows the following average composition: Loss at 105° C., 51 per cent.; volatile matter, 21 to 25 per cent.; fixed carbon, 13 to 15 per cent.; ash, 9 to 13 per cent. The nature of the volatile matter is not given, but it is probably of considerable volume and low illuminating power. H. L.

The Effect of Torsion on the Thermal and Electrical Conductivities of Metals. C. H. LEES and J. E. CALTHROP. (*Proc. Phys. Soc.*, Aug. 15, 1923.)—"The close connection which all forms of the electron theory of flow of heat and electricity in metals disclose between the conductivities k for heat and K for electricity make it desirable that these quantities should be determined for as many metals and under as many different conditions as possible in order to see the extent to which the theories agree with the facts."

It is easy to measure with accuracy the electrical resistance of a wire whether twisted or free from torsion. Immensely more difficult is it to determine the difference between the thermal conductivities of the same wire in the strained and in the unstrained state. The following method was used: The wire was stretched between two clamps in a space surrounded by a water jacket. Around the middle of the wire was wound a heating coil. When current flowed through this, the temperature fell from the coil in both directions toward the clamps at the ends. Two platinum thermometers are attached to the wire so as to give the temperatures at two points on the same half of the wire. The water jacket maintained the ends of the wire at a constant temperature. With the heating coil in action the thermometer near to it showed a higher temperature than the one near to the clamp. Upon twisting the wire, a redistribution of temperatures was brought about owing to a change in conductivity for heat, and the thermometers indicated different temperatures. The two thermometers in one case with the wire not twisted showed a difference of .24° C., and with the wire twisted a difference of .94°. From the readings of the thermometers the thermal conductivity of the wire was calculated by the use of an equation containing hyperbolic functions. It was found that both the electrical and the thermal conductivities grow less with torsion. The rate of change is considerably less for the electrical coefficient than for the thermal. In both cases the change is approximately in proportion to the twist per unit length. G. F. S.

Test for Olive Oil.—W. H. DICKHART, of the New York Produce Exchange (*Am. J. Pharm.*, 1923, **105**, 684-686), has devised the following test for olive oil. Two reagents are used, (1) a mixture of one part of concentrated sulphuric acid and four parts of absolute alcohol, and (2) a 5 per cent. solution of furfural in alcohol. A 5 c.c. sample of the oil is shaken in a test tube with 5 c.c. of the alcoholic sulphuric acid to form an emulsion; then ten drops of the alcoholic furfural are added and incorporated into the emulsion by shaking. A pink color at this stage indicates the presence of sesame oil, which interferes with this test for olive oil, and, therefore, renders further procedure useless. In the absence of sesame oil, the tube and its contents are kept in a bath of hot water at a temperature of 94° to 95° C. for ninety seconds, shaking every few seconds. The tube is now removed from the bath; 10 c.c. of cold water are added to its contents, and mixed by shaking. The tube and its contents are then permitted to stand for ten minutes. A red colored solution indicates the presence of olive oil. The other oils tested (refined cottonseed, corn, castor, chinawood, hempseed, kapok, peanut, perilla, palm, palm kernel, lumbang, mustard, rapeseed, teaseed, linseed, soy bean, cocoanut, and tobacco seed oils) yielded only a milky solution. Certain of these oils give a color prior to the addition of the water; thus a slight red is given by palm kernel, peanut, cocoanut, teaseed, and castor oils, and a greenish blue by mustard oil; however, these colors vanish and are replaced by a milky solution upon the addition of water. This test will show the presence of 2 per cent. of olive oil in another oil. If oil of rosemary be present in excess in olive oil, the volume of water added in the test should be increased to 15 c.c.; the solution becomes a dark red approaching a chocolate color, while the oil also is much darker than usual. J. S. H.

Tin as a Catalyst.—According to O. W. BROWN and C. O. HENKE, of Indiana University (*J. Phys. Chem.*, 1923, **27**, 739-760), metallic tin may act as a catalyst in the reduction of nitrobenzene to aniline by hydrogen, also in the reduction of ortho nitrotoluene and ortho nitroanisole to ortho toluidine and ortho anisidine, respectively. The tin acts better in coarse lumps than in the powdered form. Catalysis occurs at a lower temperature in an iron vessel than in one of glass. In some experiments, from 93 to 99 per cent. of the theoretic yield was obtained. J. S. H.

Automobiles in Australia. (*Machinery*, Oct., 1923.)—Australia is to-day, as it has been for some time past, the leading export market for American automobiles. The value of the cars exported to Australia in 1922 was \$23,000,000. In addition, considerable exports were made from Canada by American manufacturers having Canadian branches. Forty per cent. of the entire exports of the country were represented by eight of the best known makes of American cars.

Tin Production in 1922.—Tin, though classed among the “base” metals, has some analogies to platinum. Its high luster, practical permanence in the air and resistance at ordinary temperature to some common corrosive agents have made it of great use in the household and in some industries. Like platinum, the supply is much below the world’s needs, only a few rich deposits being known. The Cornwall mines worked for centuries, are still yielding metal. Hopes were entertained some years ago that tin might be found in quantity in the United States, but these have not been realized. In 1916, 140 tons of metallic tin were produced, but the yield has steadily fallen, until in 1922 only 1.4 short tons, all from Alaska, were reported. The tin industries in this country rely, therefore, upon imports. The largest sources for 1922 were, for metal, England 10,000 tons and Straits Settlements 47,000. Tin concentrates were imported to the amount of 12,507 tons from Chile, but as Bolivia has no ports, the material was probably from the Bolivian mines, which are among the world’s important sources. The data given in this note are taken from a compilation by B. L. Johnson, being part of the report on the “Mineral Resources of the United States” for 1922, issued in form of advance sheets by the U. S. Geological Survey. H. L.

The Diminished Intensity of the Red Part of the Solar Spectrum Observed in Equatorial Regions. L. GORCZINSKI. (*Comptes Rendus*, Oct. 22, 1923.)—On a journey to Siam and Java about 40,000 observations of the radiation received from the sun were made. Though all these have not been worked over, the author “indicates an important point that emerges from the mass of observations, to wit, the progressive diminution in the intensity of the red part of the solar radiation that shows itself on a voyage from Europe to the equator.” The measurements show a difference of about 10 per cent., that is, under the equator 45 per cent. of all solar radiation is in the red, while in Europe 50 per cent. is in that part of the spectrum. “It is to the difference in distribution of solar energy throughout the spectrum that we must attribute the characteristic effects of sunlight in the tropics. The deficiency in the red part of the spectrum, joined to the excess in the violet, can alone explain the peculiarities of animal and vegetable life in the tropics.” His results justify the author in suggesting the great desirability of studying the energy distribution in the spectrum for different regions of the earth. Of particular value would be observations made in desert regions, upon mountains, under the equator and on an island such as Tahiti. G. F. S.

On a Coil Galvanometer of Rapid Indication. W. J. H. MOLL. (*Proc. Phys. Soc.*, Aug. 15, 1923.)—The properties of more rapid indication and greater stability have been attained by modifications in design. The moment of inertia is made small by the use of a coil whose vertical length is great in comparison with its horizontal width. This reduces the period of swing. “Now when the moment of

inertia of the coil is made very small, and its weight consequently very slight, it will suffer from inevitable vibrations to a much higher degree than would be the case with a heavier coil. The desired stability has been obtained in a rather obvious way, namely, by simply stretching the coil between two metal wires, instead of suspending it." A photographically registered series of deflections shows that the instrument is very dead-beat. About two seconds were required for the deflections to reach their maximum value. This once attained, the record is free from any trace of a tendency in the coil to swing back toward its zero position.

G. F. S.

Water-cell Transmissions and Planetary Temperatures.

D. H. MENZEL. (*Astrophys. J.*, Sept., 1923.)—The radiation reaching the earth from a planet is the sum of two parts. One of these consists of waves of short length, originating at the sun and reflected by the planet. The other is the long wave radiation emitted by the planet itself. A water cell transmits the first part but stops the second entirely. The water-cell transmission is the ratio of the energy from the planet that emerges from the receiving instruments when a water cell is in its path to that which comes through without the cell. A formula is developed that connects the transmission with the temperature of the planet. This is possible because the energy radiated by the planet is dependent on its temperature.

Of the members of the solar system observed Jupiter has the largest water-cell transmission, about .67, while the moon has the smallest, .147. These temperatures are deduced—Venus, 50° C.; Mars, -16° C.; Jupiter and Saturn, -110° C., "while the moon is very hot, possibly 120° C. . . . The computed temperatures of Venus and Mars can be explained if they receive all their heat from the sun and lose it almost as fast as they receive it, cooling greatly at night. Jupiter and Saturn have higher temperatures than could be maintained by solar radiation alone, confirming the belief that the planets are hot internally."

G. F. S.

Is the Sun Responsible for the Radioactive Products of Disintegration in the Atmosphere? H. BONGARDS. (*Physikal. Z.*, July 15, 1923.)—In the air there are found products of the transformation of radioactive substances. It is no easy matter to determine by a crucial test whether these owe their origin to the earth or to bodies outside of the earth. Observations at high altitudes would be decisive only if the elevations were so great as to preclude any considerable terrestrial influence. Another way of testing would be to make observations all over the earth of the amount of emanation in the air and to extend these observations over a considerable period of time. Were the fluctuations of the quantity of emanation to follow the same course at all stations, this would argue for an extra-terrestrial cause.

The author discovered that observations made by Wright and Smith in the Philippines at Manila overlapped in time a series made by himself in Germany. He has plotted the curves showing how the quantity of emanation varied during three months. The similarity of the curves is remarkable. This by no means proves that the sun or some other distant body controls the emanation content of our atmosphere, but it does indicate that the method of simultaneous observation is well worthy of trial.

G. F. S.

The Constitution of the Upper Strata of the Atmosphere.
L. VEGARD. (*Phil. Mag.*, Oct., 1923.)—A generation ago the discovery of argon in the air unsettled the view then in vogue that all was known about the atmosphere. In the physics of the atmosphere there followed the establishment of the isothermal layer and a lengthy discussion of the escape of molecules of gases from the outermost strata. There came a time when the opinion prevailed that the highest regions contained hydrogen and helium, while nitrogen and oxygen were confined to relatively low levels. In a recent lecture before the Royal Meteorological Society, G. M. B. Dobson said: "Since the beginning of the present century, exploration by means of kites and balloons has increased our knowledge so rapidly that it may be said that we now know the general characteristics of the atmosphere up to about 20 km. with very fair accuracy. Above 20 km., however, our information practically ceases, and there seems, at present, very little hope of getting any direct observations above, say, 25 or 30 km. To obtain further information about the atmosphere above these heights, one must, therefore, look around for more or less indirect methods. There are various phenomena which occur at these altitudes which might conceivably indicate the conditions of the atmosphere, such as auroræ, meteors, night-luminous clouds, etc." Lindemann has published the results of his study of the appearance and disappearance of meteors. Lord Rayleigh is photographing the spectra of the aurora at different latitudes in England, but it is to physicists nearer to the pole that we must look for observations that will be the raw material for the elaboration of the final and satisfactory theory of the upper regions of the atmosphere. Already in the year 1923 Stormer and Vegard have made important contributions to the subject. In this, his latest paper, Vegard states that last winter he succeeded in getting spectrograms of auroræ at different altitudes. "In the first paper we saw that most of the lines appearing in the auroral spectrum are due to nitrogen, but the strongest of all lines (the green line) and three faint lines in the blue and the ultra-violet could not be found among the lines of nitrogen observed in laboratory experiments and given in tables of spectral lines. Nor can they be found among the known lines of hydrogen and helium. Already this result suggests that the green line and the other three not identified lines are due to nitrogen." Needless to say, the question cannot be resolved by a mere suggestion. Last March the author got a spectrogram of the lower edge of an

aurora with an exposure of half an hour and another of the higher parts of the same auroral display with an exposure of four hours. "The most remarkable result is, that the intensity of the green line as compared with that of the strong negative N-bands is quite as great near the bottom edge as it is 50-80 km. higher up in the atmosphere." This weighs heavily in favor of attributing the origin of the famous green line to nitrogen. If some other elementary gas gave rise to the line, this suppositional gas would have a density different from nitrogen and the relative proportions of it and nitrogen would not be the same through a height of 50-80 km. This change in the composition of the atmosphere would show itself in a difference between the two spectrograms, or, more specifically, in a variation in the relative strengths of the green line and of the unquestionable nitrogen bands.

The argument just used does not, however, rule out the possibility that some compound of nitrogen might emit the green line. Such a compound would of necessity have about the same molecular weight as nitrogen or, at most, not a greater molecular weight so that it might exist along with nitrogen in the upper atmosphere. NH_3 alone is worth consideration and the evidence of the spectrograms rules it out. "I think that the 'Geocoronium' hypothesis ought to disappear from the scientific literature, and if so the only possible interpretation of our auroral spectral analysis is to assume that also the green line is a nitrogen line emitted under those peculiar physical conditions under which the light is produced in the upper strata of the atmosphere."

The spectra of the aurora up to 400 km., or even higher, proves that nitrogen is "a predominant component of the atmosphere to its very extreme upper limit." To explain how there can be sufficient nitrogen at such great altitudes to give rise to the spectra actually observed one of these two hypotheses may be held—

(a) "We might either assume that above a certain height the temperature increased rapidly upwards," or

(b) "That the nitrogen was electrically charged by photo-electric effect and driven upwards through the effect of the electric field produced by the charged layer."

Turning to the first of these alternatives, Vegard sees that a temperature of several hundred degrees in the upper atmospheric strata would account for the relatively great density of nitrogen required in the regions of the aurora. He is compelled to reject this alternative on experimental evidence. He bombarded nitrogen at room temperature and again at the temperature of liquid air with cathode rays and found that at the higher of these two temperatures the spectrum of the gas was much more complex than is that of the aurora, while there was great similarity between the lines of the auroral spectrum and those of nitrogen at the lower temperature. "If now we have to give up the assumption of a high temperature, I can see no escape from the assumption that nitrogen in some way or other must be driven upwards through the effect of electrical forces." Such forces

are furnished by the negative charge of the earth and the positive charge above its surface. "At a certain height the positive electric mass just equals the negative, and on a sphere at this distance the electric force will be zero. Under this niveau the electric force is directed downwards, and only above it will there be an upwardly directed electric force." Somehow in the outer layers of the atmosphere electrons are removed from the nitrogen atoms, which are then left with a positive charge. The electric field of the earth urges them outward and to avoid the constant depletion of our atmosphere by a flow of nitrogen out into space the author predicates the existence of the nitrogen in the form of solid crystals. Nitrogen freezes at about 60° absolute. "But if these are the conditions under which the auroral spectrum is formed, we can understand why a nitrogen spectrum like that given out by the auroræ has never been reproduced in laboratories, for we should then have to bombard solid nitrogen dust with electric rays. . . . At present I am making preparations for experiments of this kind." How interesting it will be, if the green line is produced in these experiments!

We are then to regard this as the composition of the atmosphere—up to about 90 km. from the earth oxygen and nitrogen gases, above that dust of the two solidified elements.

The claim is made that this theory furnishes an explanation of the zodiacal light, of the blue color of the sky, of the twinkling of fixed stars and the absence of twinkling in planets, of the reflexion of electric waves and sound waves from the upper layer of the atmosphere, of the sudden change of color along a meteor track and of the increase of the maximum height of auroral rays as the equator is approached.

G. F. S.

Colorimetric Standards.—H. V. ARNY and ABRAHAM TAUB (*J. Am. Pharm. Asso.*, 1923, 12, 839-849) state that the colors produced in colorimetric determinations can usually be matched by use of two sets of solutions, each of which includes three compounds representing the three primary colors. One set is composed of half-normal solutions of cobaltous chloride, ferric chloride, and cupric sulphate, respectively, in approximately 1 per cent. hydrochloric acid. The other set consists of fiftieth-normal solutions of roseo-cobaltic chloride, ammonium chromate, and cupric sulphate, respectively, in 2.8 per cent. ammonia water. These solutions may be used as standards in the colorimetric determination of carbonizable impurities in liquid petrolatum, and in the assay of suprarenal glands for their epinephrine content.

J. S. H.



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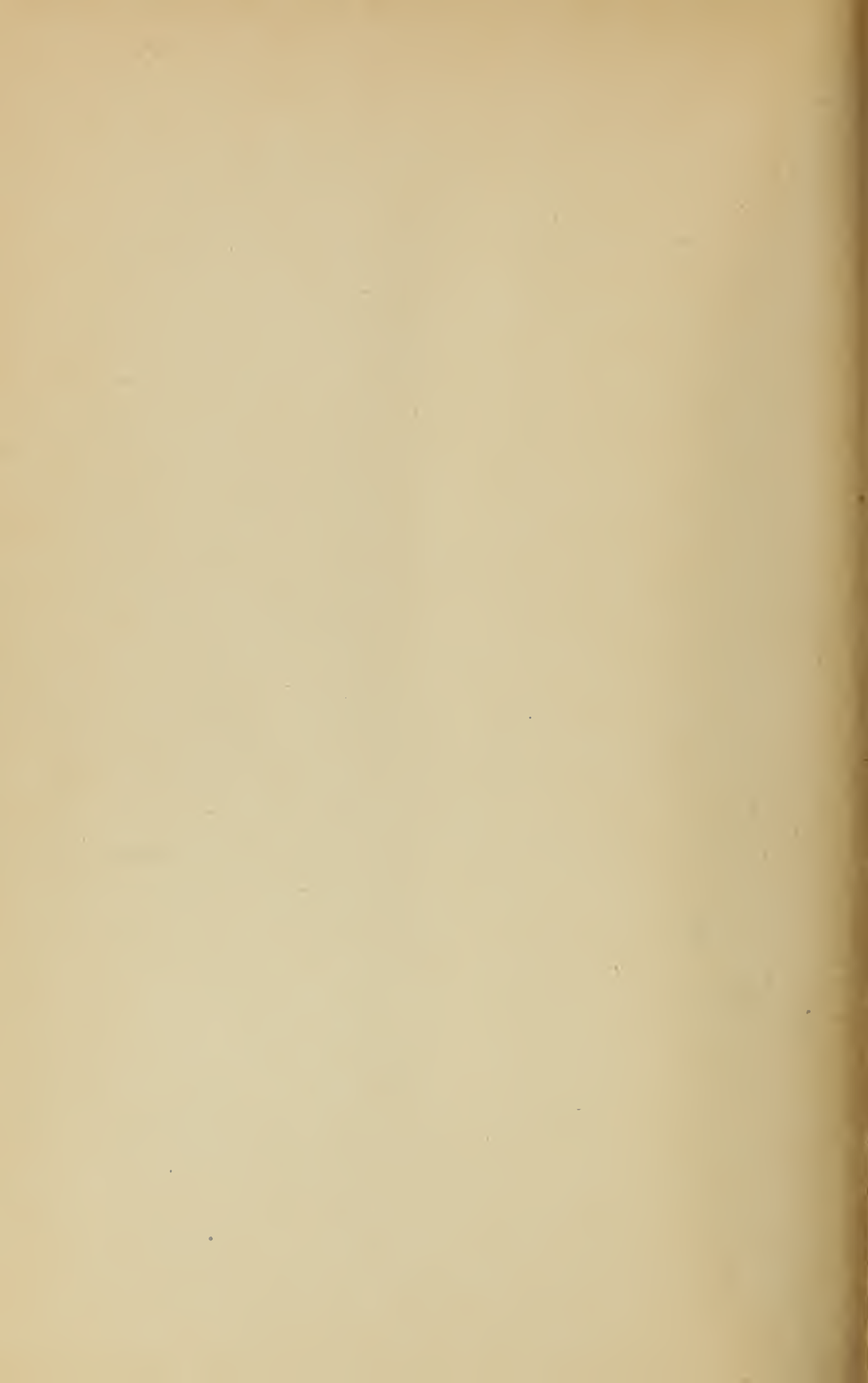
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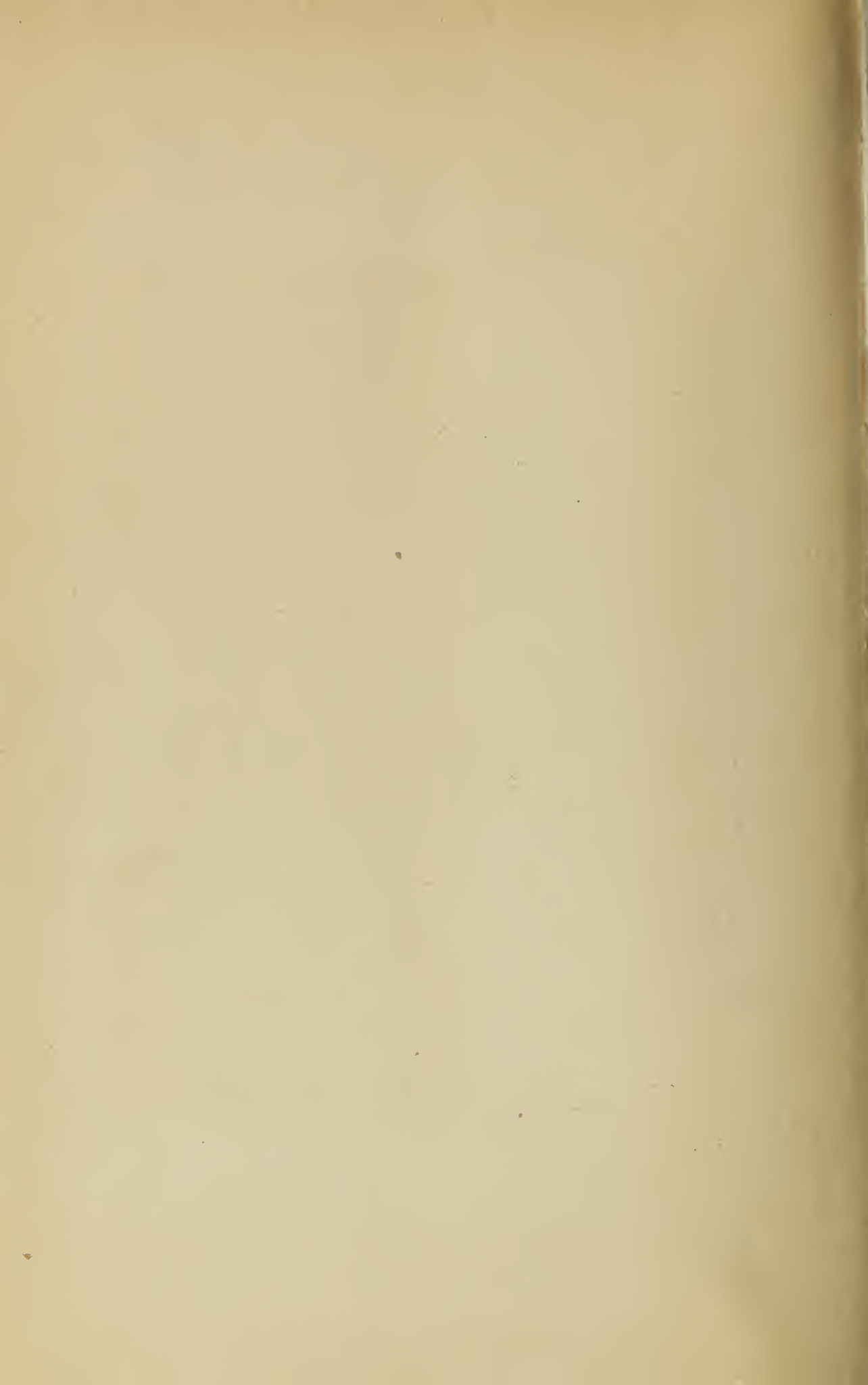
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